THE DIRECT DETERMINATION OF ORGANIC SULFUR IN RAW COALS

B. Paris

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

INTRODUCTION

The sulfur content among coals varies to some degree in total quantity and in the forms present. Generally, the forms of sulfur in coals are the inorganic (sulfide and sulfate) and the organic (a complex mixture of organo types). The sulfate content is usually present in low amounts except in some instances where weathering has converted some of the pyrite to sulfate. The sulfide form can occur as the minerals pyrite and marcasite in a rough size range from 0.25 to 200 micrometers.

The organic sulfur in coals is intimately bound to the coal molecule and is difficult to determine directly when other forms are present. The organic sulfur content in most american coals range from about 0.5 to 3%.

A total sulfur analysis will give the information on whether present SO_2 emission standards will be met upon combustion of the candidate coal. If the total sulfur is too high, and stack gas cleaning is not available, some form of desulfurization is required before this energy source can be used. Cleaning processes can remove varying amounts of the inorganic forms, and some organic sulfur may also be extracted, but for all intents, the content of this latter form may be regarded as the lower level at which coal can be beneficiated. Therefore, the baseline level of organic sulfur is important to know so that economic and time effective inorganic sulfur extractions can be applied which in turn can comply with combustion standards.

Current ASTM methods provides for the direct analyses of the total, sulfate, and sulfide sulfurs. The accepted techniques for determining the sulfur forms in coals are the ASTM[1] standard wet methods. The total sulfur is determined by the Eschka method (D3177-75) and the sulfate and sulfide by selective acid leaches (D2492-68). The organic sulfur is then obtained from the difference of the total and the two inorganic forms since no reliable direct method is available. The possible accumulation of errors and the time required ($\sim$1 1/2 days) to obtain the organic sulfur by difference has made this approach undesirable but necessary.

The precision of the organic sulfur value obtainable from this approach was calculated from numerous analyses at BMI in conjunction with precision estimates of the respective ASTM methods. At two standard deviations (95 confidence level) the precision was found to be $\pm$25%.

Instrumental methods also can be used to determine the inorganic forms and total sulfur for an estimation of the organic sulfur content. The two methods use X-ray analyses on pressed pellets of pulverized coal. In one, Hurley & White[2], use X-ray fluorescence to characterize for all of the sulfur forms by wavelength shift of the SK_β peak caused by variation in the sulfur bonding. The second[3] is discussed in an unpublished report on sulfur determination in coals, and utilizes X-ray fluorescence for total and sulfate sulfurs and X-ray diffraction for sulfide sulfur. Organic sulfur is obtained by the difference in the latter technique.

1

Both of the X-ray methods agree with corresponding wet chemical data on the same samples. The precisions of these instrumental methods therefore, are at least as good as the ASTM procedure but the time of analyses is reduced to several hours. A direct method for determining organic sulfur in coals was reported by Sutherland[4] using the electron microprobe on pressed pellets of coal.

A BMI supported program, therefore, was initiated to develop a direct and specific method for determining the organic sulfur content in coals and in the presence of the other sulfur forms. The approach taken entailed the low temperature reaction of ionized oxygen species with raw coals to yield volatile SO_x components which are the reaction products with the organic sulfur content of the coals. The SO_x products can be collected in a suitable trap maintained at low temperatures and subsequently analyzed.

Equipment

For this purpose, the instrument used for the oxidation of coals during this program was the LFE LTA 600L low temperature asher. The generator operates at a crystal controlled frequency of 13.56 MH_2 and has an output capable of delivering 300 watts of continuously variable power distributed among five separate reaction chambers. Normal ashing is carried out under continuous rough (300 1/m capacity) so as to maintain a pressure of 1 torr at an oxygen input flow of about 50 cc/min. The low temperature oxidation technique has been used to study the mineral matter content of coals. As indicated previously, the technique utilizes the oxidative properties of the reactive ionic and atomic species of oxygen which are produced when molecular oxygen is passed through a high frequency field. The ionized oxygen species are directed to the surface of the raw coal where selective oxidation of the organic content leaves the mineral matter relatively unaltered for study. The reaction produces volatile oxides of the total organic content. These products are CO, CO_2, H_2O, SO_x, and NO_x, and they are normally allowed to be discharged through the vacuum pump. The temperature of the coal surface reaction under these conditions can vary from 50 to 300°C depending primarily upon the power applied to the RF coils. Frazer et al[5] and Mitchell et al[6] used low temperature ashing of coals to study mineral stability under a variety of conditions. Although better stability of minerals were observed than that shown by the air oxidation method at 400°C, however, it was noted that pure pyrite could be oxidized at the high temperatures, 200-300°C.

To provide for the collection facility of the desired vapor species, the exit of one of the reaction chambers was rerouted to accommodate a glass trapping system. This modification is shown schematically in Figure 1. The all glass assembly, with ball joint connectors includes a stop cock (D), a trap (C) to collect the oxidized species and a connector at (E) to either evacuate during a run or to attach a gas bubbling trap for collecting the SO_2 at the end of a run. The remaining chambers were left entact so as not to interfere with the operation of the instrument.

Figure 2 shows the sample holder used for loading the sample for the oxidation run. Sample plate (A) is placed into the holder as shown after loading with coal. The sample holder containing the sample is inserted in the modified sample chamber. This overall arrangement provides ease of handling of the sample.

Reaction and Collection Procedure

A weighed sample is loaded into the sample holder onto a glass plate. The sample holder is inserted into the reaction chamber (A) through part B. The system is carefully evacuated to about 0.2 torr. As the oxidation of the coals progress, the temperature (-196 C) and pressure (1 torr) conditions permit trapping of the SO_2 and SO_3 gases as solids.

The generator is turned off after, upon visual examination, the samples appear to be completely oxidized. The oxidation time can vary from 1 to 3 hours. Helium is slowly admitted through stop cock (D) until the system can be opened to the air. A glass impinger bottle containing about 50 cc of 3% H_2O_2 solution is attached to (E). With a slow purge of He through the trap and impinger, the Dewar is removed to permit the transfer of the condensed SO_2 into the peroxide scrubber. The trap is then rinsed with a peroxide soltuion to collect the SO_3 component of the product. The two solutions are combined for sulfate analyses using the Dionex Mod 10 Ion Chromatograph.

Samples

The coals which were selected for this program were used as received except that they were ground to pass -200 mesh sieve (74 μm). Wet chemical sulfur analyses were obtained on these coals. In addition to a reproducibility study on one coal, several other coals of varying sulfur and ash contents were run to establish the suitability of this method to coals possessing varying chemical contents. The candidate coals are listed in the Table 1. along with their pertinent makeup.

The amount of coal samples taken for these runs were in the 20-30 milligram range. The resulting sulfur collections were expected to be of sufficient quantity to be determined by the analytical method to be used. Small charges were used in efforts to reduce the oxidation time to several hours. After the initial surface of coal is removed, the penetration of the ionized oxygen to the coal underlying the ash is time dependent. The possible errors introduced in the overall determination of organic sulfur due to macroscopic inhomogenieties accentuated by the small sample charges could be evaluated in the precision series.

TABLE 1. SAMPLES USED IN LOW TEMPERATURE OXIDATION STUDIES

Sample Coal	Sulfur, %				Ash, %	Moisture
	Total	Pyritic	Sulfate	Organic		
719-2 (Ohio)	6.3	1.58	2.74	1.9	14.2	3.5
719-3 (Ohio)	5.2	3.6	0.07	1.4	17.1	1.2
Hazard #4 (Kentucky)	1.52	0.66	0.04	0.82	12.8	1.1
Colstrip #2 (Western)	0.68	0.18	0.14	0.36	9.0	16.0
Beach Bottom #1 (W.Va.)	1.97	1.35	0.03	0.59	25.1	1.7
Organic Compounds						
Dithiopropionic	17.7	0	0	17.7	0	-
2-Thiophene Carboxylic Acid	24.7	0	0	24.7	0	-

3

The pure organosulfur compounds shown were also run since the results would represent ideal recovery experiments in the absence of interfering mineral forms. The sample charges used for these runs were in the 5-10 milligram range.

A study was also made of the stability of FeS_2 under the ashing conditions for coal. Oxidation of this compound yields volatile SO_2 which would be indistinguishable from that derived from the organic sulfur in coal. In addition, the pure FeS_2 was also mixed with other components to assess their affect upon its conversion. These materials include pure SiO_2, graphite, ash, and coal.

EXPERIMENTAL RESULTS

Oxidation Study of FeS_2

It was first necessary to establish conditions which prevented or reduced considerably the oxidation of pyrite to yield SO_x. The experimental conditions which were varied for the FeS_2 study included applied power to the plasma, oxygen flow, position of samples in relation to the plasma, particle size of FeS_2, and mixtures of various materials with pure FeS_2. For the runs with only FeS_2, it appears that the conversion to Fe_2O_3 and volatile SO_2 occurs under any condition. However, the severity of conversion increases directly with the applied power and inversely with particle size. The position of the sample in the chamber and the rate of oxygen flow used has minimal, if any, affect upon the oxidation of FeS_2.

The runs made using mixtures of FeS_2 with the listed additives produced mixed results. It was found that by adding graphite, SiO_2, or an organic sulfur compound to pure FeS_2 did not prevent the FeS_2 reaction with oxygen. However, admixtures with coal or fly ash appears to prevent FeS_2 oxidation. The reason for the apparent inhibition of the reaction is not known but seems to be associated with characteristics of the ash other than SiO_2. The presence of the natural ash in coals accelerates the reaction of the organic phase with the plasma. In samples containing no ash, such as graphite or an organosulfur compound, the reaction with ionized oxygen is slower.

Coal Studies

Coals were oxidized using the optimum instrumental conditions as determined to be suitable for the pyrite studies. These were found to be (1) applied power of 150 watts overall (30 watts/chamber); (2) oxygen flow at 30 cc/min; (3) and a pressure of 1 torr. The sample charge of about 25 milligrams was used. The collected sulfates were determined on a Dionex Model No. 10 Ion Chromatograph.

Using the above conditions for a coal (719-2), a series of ten runs supplied a measure of the repeatability of this technique for the organic sulfur recovery in one coal. These recovery data and precision are shown in Table 2. The ratio of the obtained/expected values allow for the calculation of the relative standard deviation of 19% at the 95% confidence level. This is slightly better than that achievable by the indirect ASTM method.

The repeatability data shown in Table 2 includes a wide range of variables. These include (1) possible inhomogeneity of small coal charges, (2) ability to duplicate reaction and collection techniques, (3) analyses of sulfate solutions, and (4) runs extended over a period of several weeks.
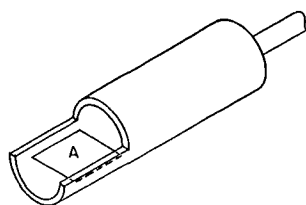
4

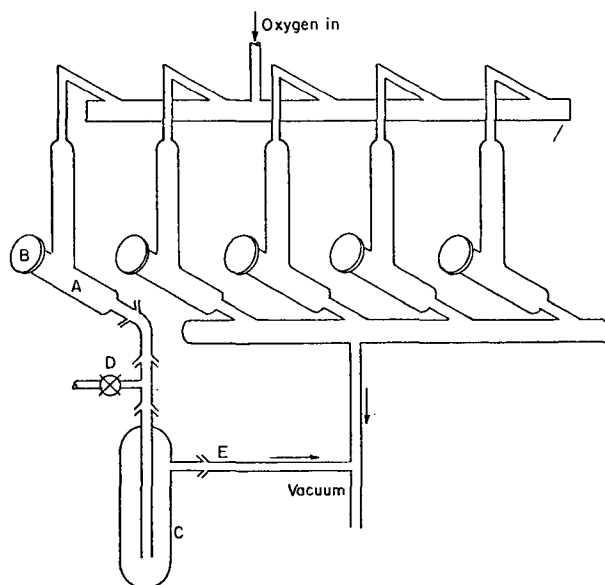FIGURE 2.   SAMPLE PLATE AND HOLDER INSERT

FIGURE 1.   SCHEMATIC OF LOW-TEMPERATURE ASHER SHOWING
MODIFIED REACTION CHAMER AND GAS FLOWS

TABLE 2. REPEATABILITY RUNS OF THE ANALYSES OF ORGANIC SULFUR
FROM OXIDATION OF 719-2 COAL

| Net Organic Sulfur, micrograms | | Ratio Obtained/Expected |
Expected	Obtained	
440	450	1.023
405	410	1.012
420	475	1.131
420	360	0.861
380	360	0.949
430	450	1.047
440	440	1.00
415	380	0.916
430	350	0.814
Mean		0.971
% SD (95%)		19.0

The second study involving coal 719-2 was to oxidize for SO_x recovery after spiking with quantities of FeS_2 in a particle size range of <37 μm. The sulfide was premixed with coal at about the 12% level so that the charge to be oxidized was about 25 milligrams of coal and 3 milligrams of pure pyrite. The mix runs were similar to the coal-only runs for the overall procedure. Results of the coal-FeS_2 runs are shown in Table 3. The relative standard deviation at the 95% confidence level is seen to be 17%.

TABLE 3. ANALYSES OF ORGANIC SULFUR FROM OXIDATION OF 719-2 COAL
SPIKED WITH PURE FeS_2

| Organic Sulfur, micrograms | | Ratio Obtained/Expected |
Expected	Obtained	
350	330	0.943
345	350	1.014
370	440	1.190
300	320	1.07
Mean		1.054
% SD (95%)		17.0

The third major experiment involved the repeatability of this technique when applied to a wide range of coals. The basis for selection included a variation in total, pyritic, and organic sulfurs as well as the ash content. The coals used for these runs are listed in Table 1.

The four coals were run in triplicate using similar procedure conditions as the two previous studies with coal 719-2. The results on the four coals are shown in Table 4. One run (colstrip) appears to be out of line, but the other ratio data seem to be well within the errors associated with either the ASTM or this direct method. The results show that this direct (oxidation)

6

method does provide a reasonable estimate of the organic sulfur content in a variety of coals.

Theoretical recoveries of S in pure organic compounds were the 90-95% range. The melting points of the two organo sulfur components are near the temperatures achieved during the oxidations. It is uncertain what, if any, affect this has on full recoveries.

TABLE 4. APPLICATION OF THE OXIDATION TECHNIQUE TO VARIOUS COALS

| | Organic Sulfur, micrograms | | | General Constituent |
	Expected	Obtained	Ratio	Range
Colstrip #2	77	123	1.6	Low pyrite, OS, Ash
	75	85	1.1	
	70	80	1.1	
Hazard #4	220	173	0.79	Medium pyrite, OS, Ash
	185	173	0.94	
	200	100	0.95	
Coshocton 719-3	330	300	0.91	High pyrite and OS,
	330	313	0.95	medium ash
	325	340	1.05	
Beach Bottom #1	180	195	1.1	High pyrite and ash,
	185	210	1.1	medium OS
	170	190	1.1	

Discussion of Problems

Other oxidized products of coals were condensed at the liquid nitrogen temperatures. Although no attempts were made to analyze the full contents of the condensed material, small amounts of ozone were present in most runs. Accidental leaks in the system during a run appears to deplete not only the ozone, but also the condensed SO_2. The resulting NO_x apparently reacts with SO_2 to form a NO-SO complex which makes it unavailable for the analytical method used.

The condensed SO_2 is reasonably stable at the trap temperature and pressure used to carry out the oxidation. The calculated loss through vaporization is about 40 nanograms per hour.

Other SO_x collection techniques were tried in efforts to simplify its recovery for analysis. One attempt included the possible catalytic conversion of SO_2 to SO_3 for its lower temperature collection. Poisoning of the platinum surface occurred about half way through the run to make this approach unsuccessful. The second attempt involved placing a NaOH-laden quartz wool plug in the rear of the holder insert. This appears to be very effective in capturing the SO_x vapor. However, to be effective the plug should be slightly moist, and this introduces some vacuum problems which have not been studied too thoroughly.

Predeposition of SO_3 (probably as H_2SO_3 or H_2SO_4) on the walls of glass system can occur at high SO_x concentrations. The deposition on the glass surfaces was very much in evidence in the investigations with pure FeS_2. Blank levels were found after coal runs.

7

CONCLUSIONS

Based upon the experimental work carried out on this program, a direct method for determining the organic sulfur content in coals has been developed. The procedure makes use of the relative ease of oxidation of the organically bound component of coals with ionized plasma of oxygen to yield volatile oxidic species peculiar to the total organic makeup. The desired products are condensed at a low temperature for subsequent analysis.

The work reported herein has demonstrated that this technique is specific for the organic sulfur content of coals within the error of the overall procedure. Repeatability runs on one coal (719-2) has produced relative standard deviations better than those obtained for organic sulfur using the different methods of ASTM. Similar precision was obtained from the same coal even when spiked with comparatively large quantities of pure FeS_2 in the particle size range of <37 μm. No sacrifice in the recovery amounts of the expected organic sulfur in the coal were indicated in these spiked runs. Successful application of this technique to other coals of varying constituents has provided some measure of the ruggedness and confidence of this approach. Also the repeatability runs indicate that the use of the 25 milligram sample charge is justified. Any error which may arise from the inhomogeneous distribution of organic sulfur in the use of small charges appears to be minimal or within the experimental precision of the method.

REFERENCES

1. ASTM, Annual Book of ASTM Standard Methods Part 26 (1976).
2. Hurley, R. G., and White, E. W., "New Soft X-ray Method for Determining the Chemical Forms of Sulfur in Coal", Anal. Chem. 46 2243-37 (1974).
3. "An XRF-XRD Method for Determining the Total and Inorganic Sulfur Quantities in Coal", Presented at the Symposium on Electron Microscopy and X-ray Applications to Environmental and Occupational Health Analyses" April 25-27 (1977).
4. Sutherland, D. C., "Determination of Organic Sulfur in Coal by Microprobe", FUEL 54 132 (1975).
5. Frazer, F. W. and Belcher, C. B., "Quantitative Determination of the Mineral-Matter Content of Coal by a Radio Frequency Oxidation Technique", FUEL 52 41-46 (1973).
6. Mitchell, R. S. and Gluskoter, H. J., "Mineralogy of Ash of Some American Coals: Variations with Temperature and Source", FUEL 55 90-96 (1976).

OXYGEN DETERMINATION AND STOICHIOMETRY OF SOME COALS

Alexis Volborth, G. E. Miller, Claudia K. Garner
and P. A. Jerabek

North Dakota State University, Fargo, North Dakota 58102

INTRODUCTION

Chemical coal analysis is divided into two categories -- the Proximate and the Ultimate. In the Proximate Analysis one determines and reports "Moisture", "Ash", "Volatile Matter", and "Fixed Carbon". In the Ultimate coal analysis one actually determines the concentration of hydrogen, carbon, nitrogen and sulfur, reports in weight percent and estimates a quantity called "Oxygen by Difference" by subtracting the sum of the above elements plus the "Ash" from hundred. (1,2, 3,4,5)

In addition, (1,2,3) the coal chemist distinguishes and attempts to determine three types of sulfur in coal (the sulfate sulfur, the pyrite sulfur, and the organic sulfur), and also tries to determine, or, at least, estimate, the Mineral Matter as originally present in coal. Chlorine, as well as several trace elements, especially those that can affect the environment (Hg, Cd, Pb, As, Se, Zn, etc.) are often also sought.

When we examine the nature of coal analysis reporting, we notice that in the Proximate category only the term "Moisture" may be equated with a chemically defined composition, namely, that of water. However, should this "Moisture" contain hydrocarbons or nitrogen volatilized at the drying temperature, then a simple weight loss method would not be sufficient to give chemically meaningful values. Thus we must describe and treat this "Moisture" (when so determined) as "weight loss" after drying in an oven at a given temperature for a certain time.

The quantity called "Ash" or "High Temperature Ash" (HTA) constitutes the total weight of incombustible residue derived from the inorganic mineral matter through dehydration, decomposition, oxidation and alteration caused by high temperature ($\sim 900^{\circ}$C) ignition of the coal in air. It is then a mixture of a heterogeneous character and is of an indeterminate and varying composition which is in some way related to the original bulk of minerals in coal. Subtracting the Total Ash in the Ultimate Coal Analysis in order to estimate the "Oxygen by Difference" introduces, therefore, indeterminate errors into otherwise stoichiometrically quite acceptable procedure of subtracting a sum of determined major elements from hundred in order to estimate the completeness of the analysis and assuming that the difference should be oxygen. One should also bear in mind that any method based on calculation by difference results in reflection of all errors in such a value.

From the standpoint of oxygen stoichiometry, the other two quantities of the Proximate Coal Analysis -- the "Volatile Matter" and the "Fixed Carbon" are of little importance because the first gives the bulk volatilized matter minus "Moisture"; the second is derived by subtracting the sum of the other three quantities ("Moisture" + "Ash" + "Volatile Matter") from hundred.

In order to attempt to quantitize the coal analysis further, we need thus a direct determination of oxygen, and once we have data for total oxygen, we must attempt to restructure the recalculation of coal analysis into a stoichiometrically more meaningful form. When this is done, the Material Balances of coal analyses should become more meaningful to the chemist and the engineer. The inadequacies of the chemical coal analysis recalculations and of the attempts to derive

from these stoichiometric data, as well as the need for a direct oxygen deter-
mination have been long recognized. We quote W. H. Ode of the U. S. Bureau of
Mines (1963)(6): "The disadvantage of such an indirect method is that all of the
errors of the other determinations are placed on the oxygen, and a Material Bal-
ance (emphasis ours) cannot be obtained to aid in checking the accuracy of the
Ultimate Analysis".

Once a direct determination of oxygen is made, the coal analyst has to
reconsider the standardized methods (3,4) of reporting and calculation of coal
analysis. For example, the comparison of "oxygen determined" to "oxygen calcu-
lated by difference", using the standard methods, can be meaningless as Given
(1975) has rightly pointed out (p. 9)(5) referring to the work of Hamrin, et al
(1975) who have used a fast-neutron activation method similar, but not identical
to ours to determine oxygen in Kentucky No. 9 coal (7). (See work by James, et
al (1976)(16), Chyi, et al (18) and Block and Dams (17)).

We have suggested in 1974(8) the use of the ultra accurate fast-neutron acti-
vation method in coal analysis. Such method was first developed by Volborth and
Banta in 1963 (9) for the analysis of rocks, lunar samples, and industrial materi-
als (10,11,12). We have further perfected and adapted this method to the analysis
of coal ash (13), coal (14), and the computerized recalculation of Material Bal-
ances (15) of six subbituminous Wyoming coals. This paper discusses specific
problems we have encountered and presents new data on a wide variety of coals sub-
mitted by the Pennsylvania State University (Dr. Alan Davis) from the well charac-
terized collection from an ERDA supported, computerized data bank (5) and some
by the Illinois State Geological Survey (Dr. Harold J. Gluskoter and Dr. Rodney
R. Ruch). We also utilize the data on the subbituminous coals from Wyoming (15)
described earlier.

EXPERIMENTAL

The method used has been described in detail elsewhere (8,9,10,11,12,14).
It consists of 20 seconds irradiation and 20 seconds counting of two samples,
a standard and the unknown, simultaneously. A special feature of our system is
the alternate switching of samples into opposite transfer channels to correct for
electronic drift and bias. The nuclear reaction $^{16}O(n,p)^{16}N$ and counting of the
resulting 6.1 and 7.1 MeV gammas with a half life of 7.3 seconds are used. The
coal samples are packed into plastic containers (rabbits) and are sealed. Mois-
ture at 105°C is determined on all samples, and the addition or loss of weight
occurring while the samples are being packed is also determined by keeping a
small sample exposed to ambient conditions for the duration of exposure. Some
dried coal powders are very hygroscopic, gaining from 0.2 to .6% in weight dur-
ing the 10 to 15 minutes of the packing procedure. Oxygen is determined on ho-
mogenized just opened "as received" samples on which moisture is determined in
our laboratory at the time of packing. Oxygen is also determined on the dried
samples (105°C). The precision of this method is ±0.2% (absolute) or better.
A simple computer program computes the oxygen percentage in "as received" and
in dried samples taking the determined moisture as H_2O into account. These data
are input into a larger computer program which uses also data provided by the
laboratory submitting the samples. These include the data of the Proximate and
the Ultimate Coal Analysis. This program recalculates, using the ASTM Standard
formulas (1,2,3), the coal analyses data based on our "Moisture", and gives the
corresponding data on "Dry" and "Dry-Ash-Free" (DAF) basis. The result is four
columns of analytical data on a coal sample, including the source data recalcu-
lated to our Moisture basis (See Table 1). The printout includes "Oxygen by
Difference" calculated in each column and Oxygen Determined on "As Received"
sample as well as on sample dried at 105°C. The determined oxygen is recalcu-
lated based on the total coal analysis data so that it can be compared in each
column with the corresponding oxygen based on other methods of reporting of coal
analyses.

10

The experiment is so designed as to permit the chemist to detect and estimate the minimum extent of oxidation of the coal in air during the Moisture determination at 105°C. This is done by comparison of determined versus back-calculated data on both samples in "As Received" and "Dry" columns.

Assuming that no other losses than water and no oxidation occur, the deter-mined oxygen in the "Dry" column should closely correspond to the calculated based on oxygen determined in the "As Received" sample. If the oxygen in the mineral matter or, if unavailable, of the ash has been also determined or estimated pro-perly and the analyses of C, H, S, N and Cl are accurate, a good sum should then be an indication of completeness of such a coal analysis. Higher oxygen determined in dry sample than that calculated based on "As Received" column should indicate oxidation or evolution of non-oxygen bearing gases (retention of more oxygen than was assumed). These processes could also balance out so that while no apparent weight loss occurs, oxidation and evolution of N_2, CO_2, CH_4, C_2H_6 etc. has taken place. The correctness of the assumption that all moisture is water can thus be checked only approximately for each coal as analyzed. It must be understood that oxidation of coal parallel with a water loss would tend to result in too low values for "Moisture" and depletion of the system of that quantity of hydrogen associated with H_2O. Low reporting of "Moisture" does also result in too high calculated values for C, H, S, and N, and, therefore, in too low "Oxygen by Difference" values causing too high summations if oxygen content is determined independently. All of these effects have a tendency to increase the oxygen content in the dried coal. Thus in most coals, one would expect an increase in determined oxygen in oven dried samples.

Decreases of oxygen content in dried coal (after the weight loss has been accounted for as water) could be due to removal of surface oxygen and replacement of it by nitrogen or coal-derived methane, for example. This effect should be mostly negligible, especially since most coal would tend to oxidize at least some-what during heating in air, masking this phenomenon.

RESULTS AND CONCLUSIONS

Thirty-three coals ranging in rank from Lignite to Bituminous coals and in-cluding subbituminous, high volatile, medium volatile and low volatile bituminous coals were analyzed and their analyses recalculated in the manner described above.

To illustrate the behaviour of these coals upon drying, the deviations between oxygen in "Dried" versus "As Received" samples were plotted in Figure 1.

Compared on DAF basis, seventeen (17) of these coals show oxygen content higher when determined in the oven dried coal (105°C) than that recalculated to this basis from oxygen determined on "As Received" (by us) coal. In twelve (12) coals no change within the precision limits of ±0.3% absolute could be observed and in four (4) coals oxygen contents lower than the precision limit were detected. Thus only about 12% of all coals analyzed showed effects of some process that may be called reduction, whereas 52% of all coals analyzed showed detectable oxidation and about 36% showed insignificant changes undectable by our method. This confirms the predicted behaviour in the last paragraphs of the previous chapter. Oxygen loss in the dried coal at 105°C is unlikely because most of the processes that can occur concurrently would tend to oxidize or increase the oxygen content if the gases evolved do not contain or contain less oxygen than the water as assumed. Only molecular oxygen if driven off the surface would cause a decrease of overall oxygen in the dried coal. It is clear that there is a positive bias in this com-parison as seen in Figure 1 and that it is not dependent on the rank of coal.

A typical recalculation of two coal analyses derived from computer printouts is given in Table 1. The first analysis is of a High Volatile A Bituminous Coal

TABLE 1

Oxygen Determination by Fast Neutron Activation Analysis in Coals
Recalculated Analyses

Proximate Analysis	HVA Bituminous Coal, West Virginia, PSOC-121			Lignite, Texas, PSOC-140		
	As Rec'd	Dry	DAF	As Rec'd	Dry	DAF
% Moisture	1.29 ±0.1°			33.96 ±0.1°		
% Ash	2.53	2.55		6.19	9.37	
% Volatile	37.86	38.38	39.39	29.59	44.81	49.45
% Fixed Carbon	58.31	59.07	60.61	30.26	45.82	50.55
SUMMATIONS	100.00	100.00	100.00	100.00	100.00	100.00

ULTIMATE ANALYSIS

	As Rec'd	Dry	DAF	As Rec'd	Dry	DAF
% Hydrogen	5.65 *1	5.57	5.72	6.91*1	4.71	5.20
% Carbon	81.16	82.22	84.37	42.93	65.01	71.72
% Nitrogen	1.72	1.75	1.79	0.75	1.14	1.26
% Organic Sulfur	0.93	0.94	0.97	0.43	0.65	0.71
% Other Sulfur	0.22	0.22	0.00	0.21	0.32	0.00
% Oxygen (by Diff)	(7.75)	(6.69)	(7.15)	(4.58)	(18.80)	(21.10)
% O (by FNAA) As Is	9.18 ± .04°	8.14	7.15 *2	47.34 ± .15°	26.01	23.95 *2
% O (by FNAA) Dried	9.17 *4	8.13 ± .07°	7.14	48.03 *4	27.06 ± .13°	25.10
Sum Inc. FNAAO (As Is)	99.03	99.02	100.13	98.59	97.87	102.88
Sum Inc. FNAAO (Dried)	99.02	99.01	100.12	99.28	98.91	104.03
% Cations,Etc,As Ash	1.36 *3	1.38	0.00	3.34 *3	5.06	0.00
Summation (As Is)	100.15	100.15		101.55	102.35	
Summation (Dried)	100.14	100.14		102.24	103.39	

* Determined by Us.   *1 Includes H from Moisture   *2 Excludes Estimated Oxygen in Ash

*3 Estimated as 54% of Ash Content   *4 Based on Moisture Content

TABLE 2

Differences Between Oxygen by Difference as Reported in Classical Coal Analysis and Oxygen Determined by NA and Oxygen Recalculated, Assuming Ash Contained 46% O

Coal No.	%O AS DIFF REPORTED "AS RECEIVED" U.S.B.M.	O DETD NA	O DIFF CALC (ASH 46% O)	% Ash
K-46566	36.6	42.34	44.34	7.70
K-46218	32.3	35.90	37.82	5.50
K-46217	31.7	36.15	37.89	6.20
K-46216	33.2	36.85	38.13	4.90
K-46565	38.8	43.28	44.19	5.40

from the Tioga Seam, Tioga No. 1 Mine, Nicholas County, West Virginia (PSOC-121). In this analysis the moisture determined in our laboratory (1.29%) is within .2% of the moisture reported (1.52%) in the Source Data (Pennstate University), the Ash is low (2.52%) and most of the sulfur is organic. Both these factors assure that the errors due to the fact that ash is not mineral matter will be small. Indeed, this analysis balances well, the oxygen based on direct determination in coal "As Received" by us as well as oxygen determined on dried coal at 105^OC corresponds closely. Thus we can say that this coal does not oxidize perceptibly during drying in air and that the moisture is probably all water (H_2O). Having not analyzed the ash, we estimate that it contained 46% oxygen, as shown by us (13) for U.S. coals and by Block and Dams (17) for some European coals. Thus it must contain 54% cations including sulfur and chlorine, and we add this amount to the summations which are first derived by adding the determined C, H, N, S, and total O% (determined by FNAA). The good second summation shows that in this coal our assumptions and approximations were justified.

The second compilation is of a Lignite from the Darco Mine, Harrison County, Texas, PSOC-140. Determined moisture (33.96%) compares closely with that reported by Pennstate (33.39%). The oxygen determined in the dried coal (105^OC), however, is 1.05% (absolute) higher than would be expected based on recalculated oxygen based on oxygen determined in the "As Received" coal. This indicates considerable oxidation and possibly evolution of gases containing less oxygen than water. This coal contains relatively little pyrite sulfur (.21%) and only 6.2% ash, so that the estimated 54% cations plus sulfur plus chlorine may be used to approximately balance the analysis when the determined oxygen values are summed up in the DAF column. Since we know that this coal has oxidized by addition of approximately 1.05% O (absolute), we can assume that the "Moisture" loss should have been reported higher by at least that amount. Assuming that all other determinations were done correctly, the use of the too low Moisture value would result especially in proportionally too high calculated value for C, H, N, and S, and thus too low values for O by Difference, which seems to be the case. This can be seen by comparison with the determined oxygen in "as received" coal calculated to DAF basis. When this oxygen value is used in the summation, one may approximately estimate whether the state of the complete coal analysis as reported is satisfactory. In this case, a bulk error of roughly about 3% is indicated. It can be due to a combination of interrelated factors, which can be a cause for erroneous moisture determination, each to a different degree. These are: a) oxidation during moisture determination; b) evolution of gases other than H_2O containing none or less oxygen than water (N_2, CO, CO_2, CH_4, C_2H_6, etc.); c) calculation errors based on faulty moisture determination which may cause a dilution effect especially on the major components, such as the carbon value, for example; d) analytical errors and bias; e) the fact that ash is not mineral matter and that pyrite sulfur should be counted as pyrite, FeS_2, as Given has pointed out (5)(pp. 31-33).

The treatment of the coal analyses described above raises several critical questions, of which only the most important can be discussed here. A few assumptions have been made above which strictly speaking are not true, and once one attempts to quantitize the coal analysis, then why not proceed logically by removing all approximations and report on a stoichiometric basis?

It turns out that this cannot be done in one step without demolishing a century-old convention due to the complex nature of computations of the classical coal analysis. The basic reason for the way a coal analysis is computed today is the variable nature of the coal substance and the inability of the coal chemist to procure a rapid and inexpensive oxygen analysis within the Ultimate Analysis Family. This situation has resulted in efforts to somehow bypass this dearth of information and turn out computations which would approximate the true chemical stoichiometric balances in the composition of coal as closely as possible. In short, the coal chemist has accepted the value for "Ash" as representative of the

13

mineral matter in the "As Received", the "Dry" and the derivation of the "DAF" columns. Also, in the calculation of the "Oxygen by Difference", the whole Ash is customarily deducted from hundred. Obviously, by definition, one cannot equate this quantity with oxygen determined directly and a quick comparison in Table 2 shows that such correlation can lead to gross errors and misunderstanding. Nevertheless, inadvertently such comparisons are often made especially in industry. This is presently the rule, and worse, when "Oxygen by Difference" is used to plot such ratios as H/C versus O/C (19,20) where by implication and the use of the chemical symbol, a very misleading picture is given.

In Table 2 we have compiled "Oxygen by Difference" data as reported by the U.S. Bureau of Mines on "As Received" basis (first column) with oxygen determined by FNAA on samples as received by us and back-calculated based on our moisture data (second column) with oxygen by difference calculated in our computer program assuming that the ash contained 46% O (third column) and subtracting only the oxygen of the ash. While comparison of the conventional "Oxygen by Difference" with oxygen determined makes little sense, this column shows improvement in terms of comparison of oxygen by difference so calculated with the determined oxygen. We seem to be thus on the right path, and able to see whether the overall assumptions were correct.

The ash portion of coals varies from a few percent to about 20 percent and more. To correct for the inadequacy of reporting and subtracting as such, Parr in 1932 (21) has proposed to estimate the Mineral Matter by the formula: % Mineral Matter = 1.08 x % Ash in Coal + 0.55% Sulfur in coal, where the factor 1.08 is the empirically derived value for water of hydration of the minerals usually found in ash.

Based on similar consideration, King, et al in 1936 (22) have derived a more accurate Mineral Matter (MM) calculation formula: % MM = 1.09 x % Ash + 0.5 x % Pyritic S in Coal + 0.8 CO_2 in Coal - 1.1 x % SO_3 in Ash + % SO_3 in Coal + 0.5 x % Cl in Coal.

These formulas have been derived from accurate stoichiometric relations considering decomposition of hydrated minerals, oxidation and formation of Fe_2O_3 from FeS_2, etc. The stoichiometry and accuracy of Mineral Matter Evaluation can be further improved by reconstituting the main minerals based on the analysis of ash. These are kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and pyrite, FeS_2, as shown by Rees (2).

The fourth column of Table 2 compares the ash contents of the coals. In our stepwise approach to the stoichiometric interpretation of coal analysis, we have found improvement if we estimate the composition of the ash. Obviously this is only an approximation and, as pointed out by Given (5), one should better use the DAF column where the influence of the mineral matter content, sulfur, and ash is further minimized. One could assume according to Parr (21) that mineral matter contains about 8% H_2O, or 9% according to King, et al (22), in which case our calculated oxygen by difference should become somewhat lower because oxygen of the water of hydration in the mineral matter should also be subtracted. Indeed, in all our cases, we obtained a better agreement with determined oxygen if this is done. All of these coals have a relatively low ash content, but nevertheless, the overall effect is about .5% less Oxygen. Taking sulfur in ash into account should further improve the agreement. Thus in many coals one may need only a recalculation of ash according to the mineral matter formulas to check stoichiometry and balance the summations. Oxygen determination gives us thus important information in characterizing coals. It may help to point out rapidly any unusual mineral composition or oxidative behaviour. Coals, where oxygen by difference value calculated by subtracting not the whole ash but only the corresponding quantity of oxygen calculated by the Parr formula agrees closely with oxygen determined, where summations balance out, may be regarded as sufficiently characterized. In

14

pyrite-sulfur-rich coals and coals with carbonates or unusual components, the more complex formula by King, et al (22) may be used. Where neither of these formulas produce a good balance, more detailed chemical work is indicated. As pointed out by us before, oxygen analysis in coal ash characterizes also the mineral matter and gives useful information on the total of all other constituents including S, Cl, etc., in ash (13).

Considerable effort has thus been spent to interpret the ash and from it the mineral matter portion of coal. One may ask why spend so much effort to evaluate a relatively minor segment of coal analysis in order to achieve stoichiometry as long as a major constituent -- oxygen -- remains undetermined. Obviously the coal chemists have done everything in order to approach true stoichiometry and be able to interpret the chemistry of coal and report the analyses in as balanced a form as possible.

We propose, therefore, that adding direct oxygen determination to coal analysis as we have done, and furthermore, determining the oxygen content in ash should bring us closer to the true stoichiometric interpretation of coal analysis. From the computer printouts of the 33 coals we have analyzed for oxygen, we can see that a single oxygen determination in a coal "As Received" quite accurately characterizes the coal as to rank, and that once the normal carbon to oxygen ratios are established for a wide variety of coals, major deviations, due to high pyrite-sulfur content or unusual mineralogy can be easily spotted (see Figure 2). This plot was obtained from the 33 recalculated coal analyses.

We distinguish stages or steps of progressively more correct approach to stoichiometric quantitation and recalculation of coal analysis. The first step is to analyze the "As Received" and "Oven Dried" coal at $105^{\circ}C$ for oxygen and to estimate the oxygen in Ash based on former work (13,17), which shows that in a great variety of normal coals, oxygen in ash varies between 44 and 48 weight percent. In 29 calculated analyses out of a total of 33 plotted, this assumption is indeed meaningful. Reasonably good summations and balances are so obtained (see Figure 1 and Table 3), except for coals with 2 to 8% S.

Secondly, When an actual oxygen analysis on ash corresponding to the coal analyzed is performed, the data should balance somewhat better. Any unusual deviations in the oxygen content of the high temperatue ash would then be a signal necessitating closer scrutiny and checks of the type of mineral matter. This approach provides a better approximation, giving us more information because actual accurate oxygen determination in coal ash furnishes us with an exact sum of the cations plus sulfur and chlorine in that ash. This means that better and more meaningful summations will result. This work is in progress.

Thirdly, to proceed further toward yet better stoichiometric balance, one can either calculate the mineral matter by the Parr formula (21), or better, by the King (22) formula as stated above. For this, however, one needs to determine total sulfur in coal in the first case, and an analysis for pyrite sulfur, CO_2, Cl, and SO_3 in coal, and SO_3 in ash and, if the content of kaolinite, pyrite and SiO_2 is to be calculated, also an analysis of ash for Al_2O_3, SiO_2, and S.

Because such a chemical approach is time consuming, and not entirely satisfactory, one may for our purposes better determine the Mineral Matter by preparing the so-called Low Temperature Ash (LTA) from the coal as proposed by Gluskoter in 1965 (23) and used by O'Gorman and Walker in 1971 (24) and further refined by Fraser and Belcher in 1972 (25) and Kinson and Belcher in 1975 (26). This method consists of radio frequency ashing of coal at temperatures of 100° to $150^{\circ}C$ and appears to give results which are perhaps the closest approximation to the true Mineral Matter in coal on "As Received" or "Dry" basis. Mineralogy of LTA ash has been recently (1976) studied by Mitchell and Gluskoter (27). An analysis of oxygen
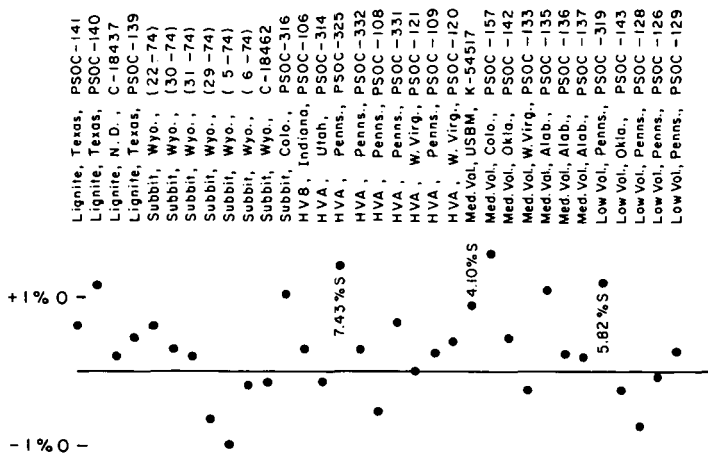
FIGURE I. PLOT SHOWING INCREASES AND DECREASES OF OXYGEN IN 33
COALS WHEN DRYING AT 105°C. % O DRY COAL MINUS % O AS
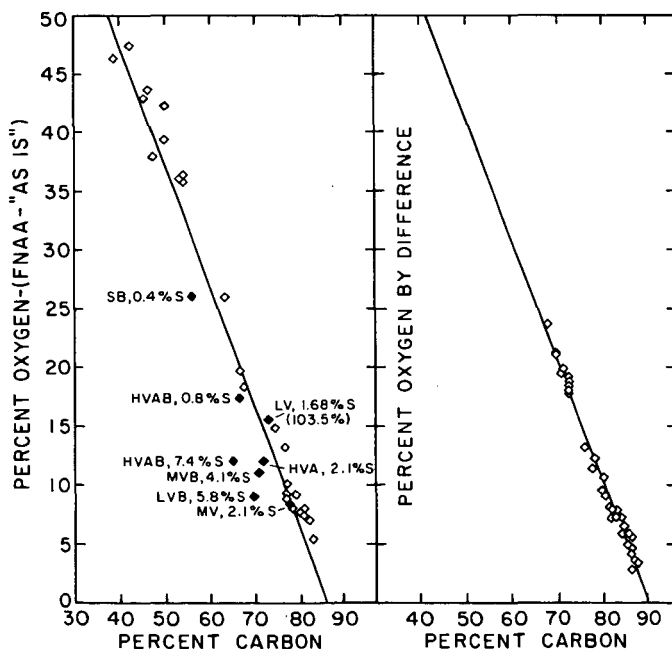RECEIVED COAL. NOTE SULFUR-RICH SAMPLES.

FIGURE 2. D/C PLOT OF 33 COALS ON "AS RECEIVED" BASIS USING
OXYGEN VALUES DETERMINED BY FNAA, AND "BY DIFF".

16

in Low Temperature Ash has been performed by us on two samples (13), however, so far we have not been able to obtain the corresponding coals. In sulfide rich coals, since pyrite is not oxidized during LTA procedure, the large error caused in the Oxygen by Difference estimation in all columns for the coals PSOC-325, PSOC-319, K-54517, in Table 3, would be minimized, if oxygen were determined directly in LTA ash. A similar approach has been taken by Hamrin, et al in 1975 (7). Assuming that the minerals in coal are not destroyed by radio frequency heating, this approach if combined with oxygen analysis in coal on "As Received" and "Oven Dried" basis as done by us may be the best way of determining the true "Organic Oxygen" in coal. We are now installing the necessary equipment in order to be able to further investigate this question.

Given and Yarzab (pp. 31-33) (5) have in 1976 emphasized the inadequacy of the ASTM Standard D 3180 reporting in sulfur-and mineral-matter-rich coals and propose the use of the British Standard 1016 Part 16 corrected procedure which distinguishes organic sulfur and recalculates the percentage of pyrite in mineral matter based on the pyrite sulfur. This is a better approach stoichiometrically as can be seen from the comparison of data given by these authors (ibid p.32). We have used at this stage the ASTM Method (see Table 3) which reports the total sulfur subtracting it from hundred on the "Dry" basis. We find that the "Oxygen by Difference" value if calculated by the British Standard Method adopted by the Pennsylvania State University agrees indeed much better with our determined values for oxygen. Therefore, where data on the type of sulfur were available, we have distinguished organic sulfur and included it in the DAF column, but have excluded the sulfate and pyrite sulfur in coal. We realize that even this approach is not fully satisfactory and intend to introduce the exact procedure recommended by Given.

In Table 3 we have compiled our data based on Pennstate data on DAF basis. Twenty-five analyses of coals not reported by us elsewhere are given. The coals are plotted in sequence based on increasing Fixed Carbon content. To save space, information on Moisture as originally reported, and as determined by us, as well as the percent Ash as reported on "As Received" basis are given in parentheses under Proximate Analysis, but do not figure in summations. These data permit the reader familiar with coal analysis and classification to make meaningful comparisons. The varying ash content is also an important criterion of accuracy expected in comparison of "oxygen by difference" with actual "oxygen determined", especially in sulfur-rich coals. In the Ultimate Analysis columns "Other Sulfur" when available is given also in parentheses, but not summed, because, as one can see in coals PSOC-325, K-54517, PSOC-137 and PSOC-319, our method permits one to estimate the approximate sulfur content based on summations. Note the retention of sulfur in carbonate-rich coal's ash (13).

It can be seen that "oxygen by difference" on DAF basis agrees reasonably well with determined oxygen in all coals that do not contain sulfur. Coals with high ash content but low sulfur also tend to balance reasonably well (see PSOC-106). Low ash coals in general give better summations (as expected) than high ash coals. The presence of high sulfur masks the effect of high ash and causes low summations if oxygen is determined. Good agreement between "oxygen by difference" and determined oxygen for "As Received" and "Dried" coal seems to indicate a well balanced analysis and minimal oxidation effects upon drying. Differences in the two determined oxygen categories tend to be mostly due to oxidation and evolution of other gases than H_2O, and, therefore, also point toward an erroneous Moisture determination due to the canceling effect of oxidation when based on weight loss.

The data on sulfur-rich coals seem to indicate that much of the sulfur, even though reported as "other" or "sulfide" sulfur is in some way bound to the coal molecule with the sulfur replacing oxygen. A part of the "inorganic sulfur" appears to compete for oxygen sites in coal in some way because all sulfur-rich coals analyzed show relatively much lower determined oxygen concentration in the

TABLE 3

OXYGEN DETERMINATION BY FAST NEUTRON ACTIVATION ANALYSIS (FNAA) IN COALS

RECALCULATED ANALYSES

PROXIMATE ANALYSIS	C18437	PSOC-139	C18462	PSOC-141	PSOC-314	PSOC-325	PSOC-316	PSOC-108	PSOC-332
% Moisture(Source)	(6.80)	(30.29)	(5.90)	(33.16)	(4.08)	(2.86)	(12.12)	(1.41)	(5.65)
% Moisture(Detd)	(7.98)	(21.06)	(5.48)	(22.14)	(4.07)	(1.30)	(12.88)	(1.64)	(3.81)
% Ash	(9.40)	(10.70)	(9.55)	(6.03)	(15.76)	(4.55)	(9.57)	(9.57)	(13.08)
% Volatile	51.07	50.89	50.39	49.15	47.91	44.68	40.97	41.31	41.45
% Fixed Carbon	48.93	49.11	49.56	50.85	52.09	55.32	59.03	58.69	58.55
Summations	100.00	100.00	99.95	100.00	100.00	100.00	100.00	100.00	100.00

ULTIMATE ANALYSIS

	C18437	PSOC-139	C18462	PSOC-141	PSOC-314	PSOC-325	PSOC-316	PSOC-108	PSOC-332
% Hydrogen	5.11	5.59	5.42	5.25	6.11	5.64	5.52	5.57	5.86
% Carbon	69.56	72.29	72.66	71.70	80.25	80.72	78.56	82.90	82.37
% Nitrogen	0.93	1.20	1.30	1.03	1.63	1.41	1.19	1.22	1.61
% Organic Sulfur	0.79	0.76	1.02	0.74	0.66	0.00	0.48	1.21	0.74
% Other Sulfur	(0.20)	(0.08)	(0.40)	(0.10)	(0.16)	(7.43)	(0.07)	(2.08)	(0.83)
% Oxygen (By Diff)	(23.62)	(20.05)	(19.40)	(20.97)	(11.35)	(12.53)	(13.14)	(9.10)	(9.45)
% O (By FNAA)As is	25.17	19.61	21.13	23.19	11.82	4.23	15.04	7.09	8.49
% O (By FNAA)Dried	25.04	22.09	20.97	23.83	11.73	5.82	16.08	6.55	9.78
Sum Incl FNAAO(As Is)	101.55	99.58	101.73	102.24	100.53	92.07	101.90	98.05	100.04
Sum Incl FNAAO(Dried)	101.32	102.06	101.57	102.88	100.39	93.59	102.94	97.52	100.33

PROXIMATE ANALYSIS	PSOC-106	PSOC-331	PSOC-109	PSOC-120	K-54517	PSOC-157	PSOC-137	PSOC-135
% Moisture(Source)	(6.40)	(5.31)	(1.88)	(1.93)	(2.30)	(1.41)	(0.71)	(0.71)
% Moisture(Detd)	(3.60)	(4.21)	(1.73)	(1.46)	(1.53)	(5.01)	(1.74)	(0.81)
% Ash	(13.46)	(4.78)	(5.05)	(5.89)	(13.60)	(6.63)	(7.00)	(4.92)
% Volatile	39.91	39.87	37.85	34.01	28.66	26.63	26.43	24.85
% Fixed Carbon	60.09	60.13	62.15	65.99	71.34	73.37	73.57	75.15
Summations	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

ULTIMATE ANALYSIS

	PSOC-106	PSOC-331	PSOC-109	PSOC-120	K-54517	PSOC-157	PSOC-137	PSOC-135
% Hydrogen	5.52	5.62	5.50	5.12	5.04	5.18	4.82	4.93
% Carbon	82.76	83.97	84.62	85.44	85.73	89.11	86.97	88.39
% Nitrogen	0.55	1.62	1.39	1.54	1.43	2.36	1.53	0.25
% Organic Sulfur	0.54	0.75	0.58	0.69	0.00	0.53	0.81	0.59
% Other Sulfur	(0.12)	(0.07)	(0.09)	(0.03)	(4.10)	(0.26)	(2.07)	(0.06)
% Oxygen (By Diff)	(10.64)	(8.04)	(7.90)	(7.21)	(7.80)	(2.82)	(5.87)	(5.84)
% O (By FNAA)As is	12.24	9.69	9.99	6.52	5.33	1.64	4.13	5.38
% O (By FNAA) Dried	12.55	10.34	10.24	7.04	4.88	3.23	4.35	6.47
Sum Incl FNAAO(As Is)	101.60	101.64	102.15	99.50	96.20	98.82	98.30	99.60
Sum Incl FNAAO(Dried)	101.91	102.30	102.40	99.92	97.08	100.42	98.50	100.70

PROXIMATE ANALYSIS	PSOC-136	PSOC-142	PSOC-133	PSOC-319	PSOC-143	PSOC-128	PSOC-126	PSOC-129
% Moisture(Source)	(0.63)	(0.94)	(0.76)	(1.85)	(0.88)	(1.24)	(0.64)	(1.67)
% Moisture(Detd)	(0.75)	(1.28)	(0.62)	(1.36)	(0.94)	(0.80)	(0.99)	(1.33)
% Ash	(2.40)	(10.08)	(6.65)	(15.40)	(8.74)	(13.40)	(6.97)	(6.23)
% Volatile	24.75	23.22	22.90	22.01	21.73	21.06	20.02	19.82
% Fixed Carbon	75.25	76.78	77.10	77.99	78.27	78.94	79.98	80.18
Summations	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

ULTIMATE ANALYSIS

	PSOC-136	PSOC-142	PSOC-133	PSOC-319	PSOC-143	PSOC-128	PSOC-126	PSOC-129
% Hydrogen	4.65	4.46	4.38	4.57	4.74	4.72	4.79	5.01
% Carbon	88.06	89.04	90.51	86.49	83.95	87.23	89.15	89.86
% Nitrogen	1.74	0.20	1.06	1.62	1.49	1.09	0.97	1.01
% Organic Sulfur	0.58	0.70	0.60	0.10	0.63	0.45	0.48	0.45
% Other Sulfur	(0.02)	(0.42)	(0.02)	(5.82)	(0.07)	(1.68)	(0.65)	(0.31)
% Oxygen (By Diff)	(4.97)	(5.60)	(3.44)	(7.22)	(4.19)	(6.51)	(4.65)	(3.68)
% O(By FNAA)As is	3.79	4.05	3.86	0.52	3.63	10.04	4.01	3.68
% O(By FNAA)Dried	4.02	4.51	3.50	1.70	3.37	9.29	3.84	3.95
Sum Incl FNAAO(As Is)	98.82	98.47	100.43	93.30	99.46	103.54	99.40	100.02
Sum Incl FNAAO(Dried)	99.05	98.92	100.07	94.48	99.20	102.79	99.23	103.29

18

DAF column than other normal coals. Thus, our method when further developed may help to evaluate the role of "Organic Oxygen" and "Organic Sulfur" in coal. We have started recalculations based on the Parr formula and the King formula to simulate the mineral matter closer in order to correct the DAF column for the effect of the additional oxygen associated with the hydrated portion of minerals. Such correction increases the proportion of C and N, and decreases somewhat the oxygen by difference values (as well as hydrogen). When this is done, more accurate "Sulfur by Difference" values can then be estimated from summations in Table 3. Thus, accurate oxygen determination permits us to estimate approximately the total sulfur when other components routinely determined in coal analysis are known. Oxygen determination in ash also aids in this case substantially, because if it is lower than the regular content (46 ± 2% O) considerable sulfur or heavy constituents in ash may be indicated.

REFERENCES

1. Bureau of Mines, Bulletin 638, pp. 1-85, 1967.
2. Rees, O. W., Rept. Investig. 220, Ill. St. Geol. Surv., pp. 1-55, 1966.
3. ASTM Standards, Annual Book, Part 26, pp. 379-401, and pp. 411-424, 1975.
4. British Standard 1016, British Standards Institution, London, 1971.
5. Given, P. H. and Yarzab, R. F., Tech. Rept. 1, The Pennsylvania State University, FE-0390-1, 1975.
6. Ode, W. H., Chemistry of Coal Utilization, Suppl. Vol. J. Wiley, Inc., pp. 202-231, 1963.
7. Hamrin, Ch. E., Maa, P. S., Chyi, L. L., and Ehmann, W. D., Fuel, Vol. 54, pp. 70-71, 1975.
8. Volborth, A., Miller, G. E., and Garner, Claudia K., Proc. Third Small Accelerator Conf., Denton, Texas, Conf. 741040-P2, pp. 199-208, 1974.
9. Volborth, A. and Banta, H. E., Anal. Chem., 35, 13, pp. 2203-2205, 1963.
10. Volborth, A., Fortschr. Miner. 43, 1, pp. 10-21, 1966.
11. Volborth, A., Dayal, R., McGhee, P., Parikh, S., Special Techn. Publ. 539 ASTM, pp. 120-127, 1973.
12. Volborth, A., Miller, G. E., and Garner, Claudia K., Am. Laboratory, Vol. 7, No. 10, pp. 87-98, 1975.
13. Volborth, A., Miller, G. E., Garner, C. K., and Jerabek, P. A., Fuel, Vol. 56, pp.   , 1977 (in press).
14. Miller, G. E., and Volborth, A., Proc. Fourth Conf. Appl. Small Accelerators, Denton, Texas, pp.   , 1976 (in press).
15. Volborth, A., Miller, G. E., Garner, C. K., Jerabek, P. A., Fuel, Vol. 56, pp.   , 1977 (in press).
16. James, W. D., Ehmann, W. D., Hamrin, C. E., and Chyi, L. L., J. Radioanal. Chem. Vol. 32, pp. 195-205, 1976.
17. Block, C. and Dams, R., Anal. Chem. Acta, 71, pp. 53-65, 1974.
18. Chyi, L. L., James, W. D., Ehmann, W. D., Sun, G. H., and Hamrin, C. E., Proc. Fourth Conf. Appl. Small Accelerators, Denton, Texas, pp.   , 1976 (in press).
19. Van Krevelen, D. W., Coal, pp. 113-20, Elsevier, N. Y., 1961.
20. Schopf, J. M., and Long, W. E., Coal Science, Adv. Chem. Ser. 55, pp. 156-195, 1966.
21. Parr, S. W., The Analysis of Fuel, Gas, Water, and Lubricants, 4th Ed., pp. 49-50, McGraw-Hill Inc., N. Y., 1932.
22. King, J. G., Maries, M. B., and Crossley, H. E., Journ. Soc. Chem. Industry, V. 55, pp. 277-281, 1936.
23. Gluskoter, H. J., Fuel, Vol. 44, pp. 285-291, 1965.
24. O'Gorman, J. V., and Walker, P. L., Fuel, Vol. 50, pp. 135-151, 1971.
25. Fraser, F. W., and Belcher, Ch. B., Fuel, Vol. 52, pp. 41-46, 1973.
26. Kinson, K., and Belcher, Ch. B., Fuel, Vol. 54, pp. 205-209, 1975.
27. Mitchel, R. S., and Gluskoter, H. J., Fuel, Vol. 55, pp. 90-96, 1976.

NEUTRON-GAMMA TECHNIQUES FOR ON-STREAM ANALYSIS OF COAL

J. R. Rhodes

Columbia Scientific Industries, P. O. Box 9908, Austin, Texas 78766

Rapid analysis of coal is required during buying and selling and for process control of coal preparation plants, coal-burning power stations and coal conversion plants. Modern process control is concerned not only with optimization of process parameters but also with minimization of environmental pollution. The components whose determination is most often needed are calorific value, total ash, moisture content and sulfur content. Other important components include ash fusibility, boiler fouling index, ash electrical conductivity, and nitrogen, chlorine and alkali metals contents.

Process control requires that the analytical result be available within the response time of the process being controlled. For the bulk solids considered here, such times are usually in the range 5 to 50 minutes. Thus, any analysis method, however rapid, is ruled out if it requires sampling and sample preparation times longer than this. Neutron-gamma techniques are non-destructive, non-contact, instrumental methods for elemental analysis of solids and liquids. They are unique in that the analyzed sample volume can be of the order of 30 cm cube. This is because the mean free paths of the incident neutrons and excited characteristic gamma rays in solids and liquids have that order of magnitude. Coal samples of these dimensions can have maximum particle sizes of up to 1 to 2 cm and still be "representative". Therefore sample preparation, if necessary at all, need only take a few minutes. In addition, the methods are amenable to continuous analysis of moving material. Thus even larger amounts of coal can be scanned during a given measurement time with consequent improvement of "sampling statistics".

Since these methods are specific to elements, satisfactory correlation must be assumed or proved between the desired components and the elements determined. Obviously there is no problem with elemental components such as sulfur, nitrogen and chlorine. Calorific value is well correlated with carbon and hydrogen content.[1] Ash content is correlated with the concentrations of the ash-forming elements, the major ones of which are Al and Si.[2] Ash fusibility is correlated with the basicity ratio which is a function of the basic and acidic oxides of the ash-forming elements (Al_2O_3, SiO_2, CaO, Na_2O, K_2O and to a lesser extent MgO and FeO_x). Moisture is correlated with hydrogen as long as the C/H ratio of the particular coal remains constant.

Early investigations of neutron-gamma methods concluded that, for most key analyses, a neutron generator had to be used as the source and this was not considered practical for plant conditions.[3,4] Consequently an on-stream coal-ash monitor based on X-ray backscattering, and using a small, sealed radioisotope X-ray source, was developed[3] and has been in commercial use for about 10 years. However, the X-ray method is limited to total ash monitoring and the coal must be sampled, dried and crushed to less than about 5 mm particle size before analysis. The availability in 1967 of Cf-252 sealed radioisotope neutron sources rekindled interest in neutron-gamma methods and an on-stream sulfur monitor[5] and moisture meter[6] have now been developed to plant prototype stage. Other feasibility studies for multielement coal analysis have been conducted[7-10] but, to our knowledge, they have each been restricted to consideration of a single neutron-gamma method and have not been able to demonstrate feasibility for analysis of more than a few of the vital elements necessary for proper on-stream analysis of coal.

The studies reported in this paper show that it is possible to determine essentially all of the major and minor elements in coal necessary for process control by not restricting oneself to a single neutron-gamma technique. Furthermore, the optimum nuclear reaction for each element can then be chosen, so reducing the demands

on the gamma-ray detector and electronics. This in turn makes possible the use of the simplest and most practicable instrumentation for reliable plant operation.

NEUTRON-GAMMA METHODS AND INSTRUMENTATION

Methods

In neutron-gamma methods of analysis neutrons from a suitable source bombard the sample, exciting nuclear transitions. Excited nuclear states decay at once with emission of "prompt" gamma rays whose energies are characteristic of the excited nucleus and whose intensities are proportional to source strength, element concentration and spectrometer efficiency, as in other methods of spectral analysis. If the sample and source are separated, the prompt gamma-ray emission stops but "delayed" or "activation" gamma emission is usually still present. The intensity of the activation gamma rays is, as before, proportional to element concentration but also falls off exponentially with time according to the half-life of the product nucleus. The incident neutrons can have any energy from several MeV ("fast" neutrons) to less than 0.1 eV ("thermal" neutrons). Fast neutrons excite several useful reactions and thermal neutrons excite several others. So in practice we can speak of four types of neutron-gamma analysis: (1) fast neutron-prompt gamma; (2) fast neutron activation; (3) thermal neutron-prompt gamma; and (4) thermal neutron activation.

Although the cross sections for producing prompt gamma rays are relatively high, yielding large signals, their detection must take place in the presence of a high background from the nearby neutron source. The design of a practical prompt gamma-ray analysis system is, therefore, a compromise between high detector background and geometrical losses due to the bulky neutron and gamma-ray shielding required. The main advantage of neutron activation is that the source and sample can be separated, enabling the signal to be measured at low background. Activation gamma spectra are also less complex. The cross sections for activation gamma emission are generally lower than those for prompt gamma emission but the much lower background outweighs this, resulting in activation often being the preferred reaction if a choice exists. Table I lists the main characteristics of the preferred methods for analysis of the important elements in coal.

Instrumentation

A neutron-gamma analyzer consists essentially of a neutron source, a gamma-ray spectrometer and a sample presentation system. Instrumentation suitable for in-plant operation must be ruggedly constructed and packaged, and must be capable of operating reliably over long periods, unattended. It should, therefore, be as simple as possible, use solid state circuitry in preference to vacuum tubes, have the minimum number of moving parts, avoid vacuum systems and ultra-high voltages, and operate without the need for special supplies such as liquid nitrogen, cooling water and compressed air.

Three types of neutron source exist, nuclear reactors, neutron generator tubes and radioisotope sources. Radioisotope sources have advantages of small size, rugged, solid state construction and stability of output. However, their steady decay has to be corrected for and forces renewal after about two half-lives. Also they cannot be "turned off" and they provide a potential radioactive contamination hazard in the event of an accident. Since Cf-252 sources have withstood being dropped 20,000 feet down a borehole and fished out without developing radioactivity leaks, we feel that the combined probability of an accident plus serious contamination is very low. Since it will be shown that the required analyses can be performed using relatively low neutron outputs ($< 10^9$/sec) the need to "turn off" the sources doesn't arise. Only 1 or 2 feet of biological shielding is required for neutron sources of this strength and they can be handled for short periods without any shielding, using the proper tools. As for the radioactivity induced in the sample

TABLE 1

PREFERRED NUCLEAR REACTIONS FOR IMPORTANT ELEMENTS IN COAL

Element	Nuclear Reaction	Threshold Neutron Energy	Main Gamma Energies (MeV)	Half Life
Hydrogen	(n,γ)	Thermal	2.23	Prompt
Carbon	$(n,n'\gamma)$	4.8 MeV	4.43	Prompt
Nitrogen	(n,γ)	Thermal	10.83,10.32	Prompt
Sodium	$\{\ ^{23}Na(n,p)^{23}Ne$	3.75 MeV	0.44	38 sec
	$^{23}Na(n,\gamma)^{24}Na$	Thermal	1.37,2.75	15.0 hrs
Aluminum	$\{\ ^{27}Al(n,p)^{27}Mg$	1.9 MeV	0.84,1.01	9.5 min
	$^{27}Al(n,\gamma)^{28}Al$	Thermal	1.78	2.31 min
Silicon	$\{\ ^{28}Si(n,p)^{28}Al$	3.96 MeV	1.78	2.31 min
	$(n,n'\gamma)$	1.9 MeV	1.78	Prompt
Sulfur	(n,γ)	Thermal	5.42	Prompt
Chlorine	$\{\ (n,\gamma)$	Thermal	6.11	Prompt
	$^{37}Cl(n,\gamma)Cl^{38}$	Thermal	1.64 and 2.17	37.3 min
Potassium	^{40}K	Natural Radioactivity	1.46	1.3×10^9 yr
Calcium	$^{48}Ca(n,\gamma)^{49}Ca$	Thermal	3.1	8.9 min
Titanium	$^{50}Ti(n,\gamma)^{51}Ti$	Thermal	0.32,0.93	5.8 min
Manganese	$^{55}Mn(n,\gamma)^{56}Mn$	Thermal	0.85,1.81,2.1	2.58 hrs
Iron	$\{\ (n,\gamma)$	Thermal	7.63	Prompt
	$(n,n'\gamma)$	0.86 MeV	0.84	Prompt

by neutron irradiation, it is both short-lived and completely negligible, being a few orders of magnitude lower than can be detected by a dose rate meter and of the same magnitude as natural K^{40} radioactivity. Two sources were used in the present study, a 38 Ci Pu^{238}-Be fast neutron source (half-life 86 yrs) and a moderated, 100 μg Cf^{252} thermal neutron source (half life 2.6 yrs).

The second major component of an analysis system is the gamma-ray spectrometer which consists essentially of an energy-dispersive gamma-ray detector, HV supply, pulse amplifiers, an analog-to-digital converter, and a multichannel analyzer with microcomputer for spectrum acquisition and data analysis. High resolution, liquid nitrogen cooled Ge(Li) gamma-ray detectors have been proposed for coal analysis and can resolve even the most crowded gamma spectra. However, these detectors are relatively easily and permanently damaged by neutron absorption or loss of cryogenic cooling. Also their gamma-ray detection efficiency is an order of magnitude lower than that of the more rugged NaI(Tl) detector and they cannot operate at count rates above about 10^4/sec without severe resolution degredation or signal losses due to dead time. Scintillation counters using NaI(Tl) crystals (or CsI(Na), CsI(Tl), CaF_2(Eu), etc.) do not require cooling or vacuum and are available in large sizes suitable for efficient gamma-ray detection. They can operate at count rates up to about 10^5/sec without special electronics (10^6/sec with special electronics). They are little affected by neutrons and the effects (induced radioactivity) are reversible and do not seriously hinder operation. The crystal-photomultiplier assembly must be temperature controlled to about $\pm$ 1°C and not subjected to thermal shock. The gamma-ray energy resolution (in the range 5 to 8%) is adequate to resolve most gamma energies of interest. All the experiments reported here were conducted with a NaI(Tl) detector and standard electronics, a schematic of which is shown in Figure 1. Figure 2 shows a schematic of one measuring head indicating the relative position of source, sample, detector and shielding. Figure 3 shows a photograph of a typical measuring head and the electronic system suitable for operating three such heads. A minimum of three heads would be required if all four neutron-gamma techniques were needed for a particular multielement analysis.
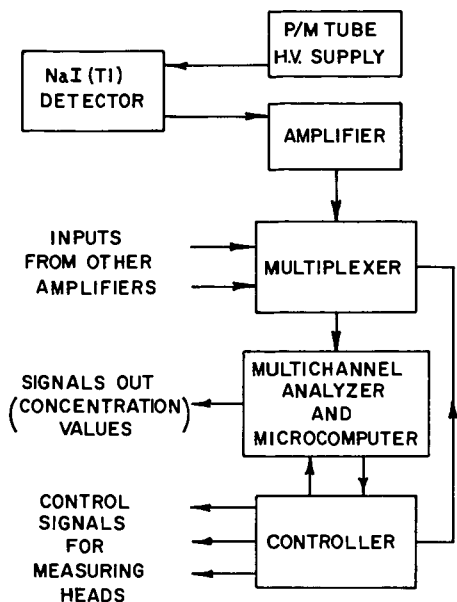
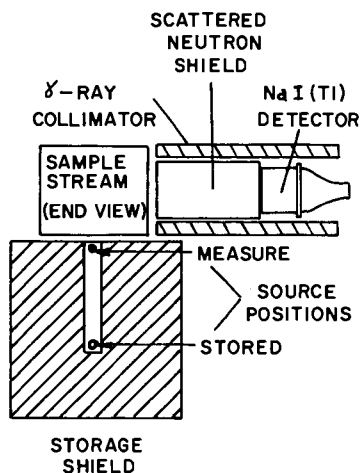FIGURE 1   SIMPLIFIED ELECTRONIC SCHEMATIC

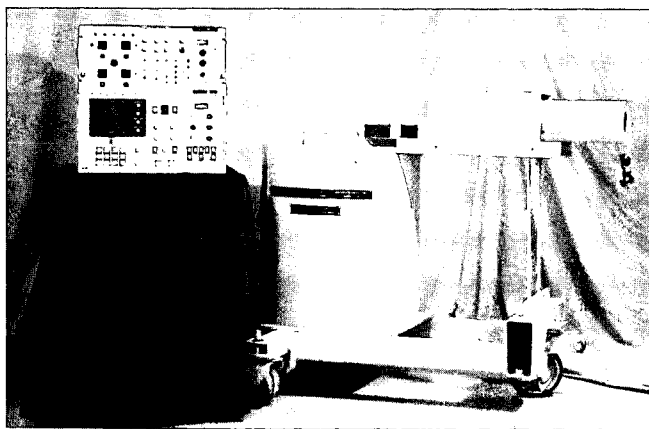FIGURE 2   SCHEMATIC OF MEASURING HEAD

FIGURE 3   PHOTOGRAPH OF MEASURING HEAD AND ELECTRONIC SYSTEM

24

The sample presentation used in this study consisted of the manual placement of 20 Kg samples (in 28 in. dia. cylindrical holders). A continuous presentation system would consist of a means of transporting a stream of coal having well-defined dimensions ($\sim$ 30 cm x $\sim$ 30 cm cross section) past the measuring heads at approximately 5 to 50 cm/sec. The coal stream could be enclosed suitably (e.g., in a sheet metal tunnel) since the incident neutrons and emitted gamma rays easily penetrate thin engineering materials. Representative sampling and splitting the primary plant streams to yield such an analytical stream is routine in coal engineering.[11]

EXPERIMENTAL RESULTS AND DISCUSSION

Sensitivity studies were made using simulated coal samples consisting of sugar spiked with (1) $MgO + SiO_2$, (2) $Fe_2O_3 + S$, (3) $Na_2SO_4 + Al_2O_3$, (4) $CaCO_3 + NH_4 NO_3$. In addition unspiked sugar and a sample of -1/2 in. bituminous coal were examined. All the samples were measured using each of the four neutron-gamma methods. All the gamma-ray spectra obtained were relatively simple and comprised a few prominent, well-resolved peaks. Thus data analysis consisted simply of integrating each peak and subtracting background measured in a group of adjacent channels. Table II summarizes the results. The neutron-gamma method used in each case is listed along with the sensitivity obtained. Also, typical concentration ranges for these elements in U.S. coals are given. It is seen that the sensitivities obtained are adequate for all the elements tested.

<div align="center">TABLE II</div>

<div align="center">PRELIMINARY RESULTS OF SIMULATED COAL ANALYSIS</div>

Element	Concentration Range in U.S. Coals	Method Used	Gamma-Ray Energy (MeV)	Source	Measurement Time (sec)	Sensitivity (1 Std. Dev.)
H	$\sim$ 5%	Thermal n. Prompt γ	2.23	Cf-252	500	0.01% H
C	65-75%	Fast n. Prompt γ	4.43	Pu-Be	500	0.2% C
N	$\sim$ 2%	Thermal n. Prompt γ	10.32, 10.83	Cf-252	500	0.1% N
Na	0.01-0.2%	$Na^{23}(n,\gamma)Na^{24}$ Thermal n. act^n	2.75	Cf-252	300 + 300*	0.01% Na
Al	0.6-2.5%	$Al^{27}(n,\gamma)Al^{28}$ Thermal n. act^n	1.78	Cf-252	300 + 300*	0.003% Al
Si	1-6%	$Si^{28}(n,p)Al^{28}$ Fast n. act^n	1.78	Pu-Be	300 + 300*	0.05% Si
S	0.2-7%	Thermal n. Prompt γ	5.42	Cf-252	500	0.03% S
Ca	0.1-1.8%	$Ca^{48}(n,\gamma)Ca^{49}$ Thermal n. act^n	3.09	Cf-252	300 + 300*	0.1% Ca
Fe	0.4-3%	Thermal n. Prompt γ	7.63	Cf-252	500	0.1% Fe

Neutron-gamma techniques yield linear calibrations of gamma peak area vs element concentration from the detection limit to 100%. This and other work with the same equipment[12] showed that heterogeneity and matrix absorption effects, common in other instrumental analysis techniques, were negligible. One exception to this is thermal neutron absorption caused by increasing hydrogen content of the sample. The effect is proportional to the 2.23 MeV H peak area, and monitoring that peak can yield a satisfactory correction. Alternatively, it is possible to monitor the thermal neutron flux in the sample.

---

*Activation time plus counting time.

The only other interferences found were peak overlaps in the gamma-ray spectra. These are all readily resolved and present work is concentrated on finding the simplest methods to do this. We have shown that one such interference, between Al and Si, is resolved by using two neutron-gamma techniques. Al and Si activate to the same isotope, Al^{28}, so that neither gamma energy nor time resolution can be used to discriminate between the signals. The dual source technique[13] uses two separate irradiations, by different sources, of similar samples. In one case fast neutrons preferentially excite Si and in the second, thermal neutrons preferentially excite Al. Solution of a pair of simultaneous, linear equations provides accurate Al and Si concentrations. In other interferences, for example, Mn on Al, Si and Cl, Ca on Na, the interfering species emits other gamma rays with a fixed intensity ratio to the interfering one. Measurement of the intensity ratio, which is an instrumental constant, and the intensity of the resolved lines is a straightforward way to correct for this type of interference. A microprocessor-based calculator interfaced to the multichannel analyzer then provides a ready method for solving the linear equations and yielding concentration data suitable for direct digital readout and plant control.

REFERENCES

(1) Mott, R. A. and Spooner, C. E., Fuel 19, 236-31 and 242-51 (1940).
(2) Loska, L. and Gorski, L., Koks, Smola, Gaz 18 (2), 52-56 (1973).
(3) Rhodes, J. R., Daglish, J. C. and Clayton, C. G., "A Coal Ash Monitor with Low Dependence on Ash Composition", in Radioisotope Instruments in Industry and Geophysics I, IAEA, Vienna 1966, pp. 447.
(4) Rhodes, J. R., Berry, P. F. and Sieberg, R. D., "Nuclear Techniques for On-Stream Analysis of Ores and Coal", ORO-2980-18, USAEC (now USERDA) September 1968.
(5) Stewart, R. F. et al., "Nuclear Meter for Monitoring the Sulfur Content of Coal Streams", U. S. Bureau of Mines TPR 74 (1974); RI 8038 (1975); and MERC/RI-76/4 (1976).
(6) Hall, A. W. et al., "Continuous Monitoring of Coal by a Neutron Moisture Meter", U. S. Bureau of Mines RI 7807 (1973).
(7) Rasmussen, N. C. et al., "The Analysis of Coal Using a Cf-252 Source", Trans. ANS 14 (2) p. 931 (1971); also Trans. ANS 10 (1), p. 29 (1967).
(8) Parsignault, D. R. et al., "A Prompt Gamma-Ray Coal Analysis System", CONF 710402, Augusta, Ga., 1971, p. IV-40.
(9) Californium-252 Progress 20, January 1976, p. 37.
(10) Duffy, D. et al., "Analysis of Synthetic Coals with Capture Gamma-Rays Using Cf^{252}", Trans. ANS 24, p. 117 (1976).
(11) Hall, D. A., "Automatic Sampling of Coal", Colliery Engineering; Part 1, February 1963, p. 55, Part 2, March 1963, p. 105, Part 3, April 1963, p. 143.
(12) Taylor, M. C., "A New Method for Field Analysis of Plastic Concrete", CERL Technical Report M-64 (1973).
(13) Taylor, M. C. and Rhodes, J. R., "Analyzing Process Streams by Neutron Activation--A Dual Source Technique", Instrum. Technol. 21, 32-35, February 1974.

An ASTM Approach to the Standardization
of New Techniques for Coal Analysis

by W.J. Montgomery

Energy Research Laboratories
CANMET
Department of Energy, Mines & Resources, Canada
c/o 555 Booth Street,
Ottawa, Ontario K1A 0G1

ASTM Committee D-5 on Coal and Coke is responsible for development of
specifications for coal and for coke produced from coal; the development of methods
of sampling, analysis, and testing; the development of specifications for classifi-
cation of coals on the basis of chemical and physical characteristics; the standard-
ization of terminology; and the promotion of research and dissemination of knowledge
in these fields. The work of the committee is co-ordinated with other ASTM commit-
tees and other organizations having common interests.

The committee is made up of producers, users and those whose general inter-
ests are in coal as a resource and its utilization. The standards produced by the
committee reflect this balance of membership. To ensure that standards are kept up-
to-date in the opinion of those who use them, the Society dictates that all standards
must be reviewed every five years and, if they are neither reapproved nor revised,
they must be withdrawn as standards. To further ensure that modern standards are
available when required, an ad hoc task group is appointed by the committee at regu-
lar intervals to study existing standards, to critically evaluate them in the light
of current usage and to recommend the needed changes. The task group may also sug-
gest the standardization of tests necessary to coal-conversion processes such as
gasification and liquefaction.

ASTM Standards for coal and coke have never been static, nor are they con-
sidered to be the last word; they are, however, the best available at the time.
Revisions to existing methods are made frequently within the five-year review period.
All revisions other than those of an editorial nature must be approved by letter
ballot of the committee before they are accepted.

Analytical procedures for coal and coke may be divided into two groups:
those based on empirical methods developed in the early years of this century, and
those based on stoichiometric chemical reactions. Empirical test methods, such as
moisture, ash and volatile matter, were developed in the industry to fulfil a com-
mercial need and finally they became standards. These tests remain much the same
today as when they were adopted 60 or 70 years ago. Using these tests, a consider-
able bank of data has been accumulated, which can be compared with current analyses
carried out by essentially the same methods.

On the other hand Standard methods based on stoichiometric reactions have
progressed rapidly in the past 10 to 15 years. Ash analysis, i.e. mineral analysis
of coal and coke ash for the ten major constituents, has progressed from the time-
consuming wet chemical procedures, through a combination of wet chemical, flame-
photometric, and spectrophotometric methods which resulted in the adoption of D 2795
in 1969. The latest editorial revision was in 1975. In the intervening time it was
realized that better and less time-consuming methods were available and work is well
advanced in developing an atomic-absorption procedure using a lithium tetra-borate
fusion technique. The new method has good precision and can be carried out with
relative speed. One of the major difficulties in this program has been the lack of
standard reference samples for the major elements present in coal ash. Standard

Reference Materials for total sulfur in coal, mercury in coal and fly-ash and several other trace elements in coal and coal ash have been available for some time from the National Bureau of Standards. Steps are being taken to request NBS to prepare Standard Reference Materials for the major elements in coal and coal ash.

Concern with the environment and laws governing the levels of allowable pollution from the use of coal have prompted the standardization of analytical methods for the determination of these pollutants. Many analytical methods have been developed by governmental agencies and universities, using a wide range of techniques. The task of filtering out the best and most practical methods with reference to coal has fallen on Committee D-5. Many of the proposed methods require expensive and highly sophisticated instrumentation. We in ASTM feel that an acceptable standard method must be within the financial reach of those expected to use it. Very few laboratories have the capabilities of carrying out certain test methods because of the high cost of instrumentation. Atomic absorption spectrometry is now considered quite common on this continent, and is no longer considered exotic. The principles are well established and most laboratories have operating experience. On this assumption we feel justified in standardizing methods using this approach. We still have reservations when it comes to the standardization of methods based on X-ray fluorescence (XRF), neutron activation etc. There is no doubt that these methods will be acceptable in the near future as techniques improve and the costs come within the reach of commercial laboratories.

Many new techniques have been suggested for coal analysis; one is the micro-determination of carbon and hydrogen which has proven to be a valuable tool in research where the amount of sample may be limited to a few milligrams. The micro method requires that the sample weight be in the order of 10 milligrams. To extract a representative sample of that size from a laboratory sample of coal (-0.250mm, #60 U.S. Standard Sieve or even -0.074mm, #200 U.S. Standard Sieve) is difficult if not impossible. A semi-micro technique can probably be developed. However the Liebig method as described in D 3178 will suffice until a new method is developed.

A semi-micro method for the determination of nitrogen in coal is being studied at present. As this procedure is faster than the Kjeldahl method, requires less space and is less costly, it is likely to receive early acceptance as an alternative to D 3179.

Many methods have been proposed for the determination of sulfur in coal and coke, and to-date only a few have been found suitable for standardization. The basic method with which all methods are ultimately compared is the Eschka Method. The Bomb-washing and the High-temperature-combustion methods are acceptable alternatives. Combustion methods, using induction or glow-bar-heated furnaces to convert the sulfur compounds to SO_2 have been examined and found to be unsuitable as standard methods. It is reported that newer designs of this type of equipment are much more reliable. Experience indicates that frequent standardization against analysed standards is advisable.

Also with reference to sulfur determinations, improvements have been incorporated in the method of determining pyritic sulfur in coal. In the present method, D 2492 Forms of Sulfur, pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid followed by a titrametric determination of iron as a measure of pyritic sulfur. Appropriate corrections are made for non-pyritic iron.

As an alternative procedure the pyritic iron may be determined by atomic absorption.

Over the years D-5 has been presented with the problem of developing a standard to cover coal stockpile inventory which is of concern to utilities and other large users of coal. This task has been carried out for years by time-consuming

measurement of the pile to determine its volume as accurately as possible followed by an also-time-consuming sampling program to determine the average density of the coal at varying depths in the pile. From these measurements, which were rough at best, the tonnage was calculated. We have now been asked by CAPCO (Central Area Power Coordinating) Group, to co-operate in their program to develop a standard. This group, some of whose members are from D-5, are studying the feasibility of the use of a nuclear probe and scaler which would operate on the basis of gamma radiation and reflection to accomplish the required measurements. A second approach under consideration is the use of a radio-echo device. D-5 cannot participate directly in the development stages but will be interested in standardization when the necessary instrumentation is developed.

D-5 has an ash analysis standard, and a standard method for the preparation of ash. We have now been requested to develop a method for the preparation of an ash (fly-ash) which is non-standard, to simulate ash produced under pulverized fuel burning conditions. Ash produced under such conditions would be vastly different from that prepared under the standard conditions specified in D 2795, i.e. from room temperature to 500°C in one hour and 750°C in two hours, and finally ignited to constant weight at 750°C in a well-ventilated muffle furnace. Ash produced under the conditions prevailing in a pulverized fuel burning system would be subjected to much higher temperatures, thus causing the volatilization of elements such as sodium. It is also true that some of these volatile constituents may recombine to varying degrees, producing compounds not normally found in the standard ash. A group on the west coast has asked for our co-operation in this project, which will involve the ashing of a relatively large sample of coal under specific conditions. The specific conditions necessitate the use of a specially designed mini-furnace to burn the coal in a pulverized form to produce the simulated ash. The design and construction of the furnace will be undertaken by this group.

The group representing utilities and manufacturers of electrostatic precipitators require an ash prepared in this manner so that, when a chemical analysis, resistivity measurements and other tests are made, the data so obtained can be correlated with the ash (fly-ash) present in the stack from which they are attempting to remove the particulate emissions. An ash prepared by conventional standard methods does not meet these requirements.

Fuel calorimeters manufactured today are highly sophisticated as compared to those in use in the thirties. While thermometers may still be used to measure temperature-rise they have in many instances been made superfluous by the introduction of thermisters. Most modern adiabatic calorimeters have both, thermometers manufactured to ASTM standards and thermisters with digital read-out, and in some instances a print-out attachment is added. The use of this modern instrumentation, while not sanctioned by ASTM, is found to be very satisfactory in helping to eliminate the human element.

The manual operation of the cold - and hot-water valves in an adiabatic calorimeter has been superseded by automatic operation. This new instrumentation is good and exceedingly reliable.

The determination of volatile matter in coal and coke can now be carried out in duplicate, using equipment programmed to lower the crucibles into the furnaces at the required rate, to hold them there for a given time and then to withdraw them.

While many of the methods have remained basically the same for many years, automation has assisted the analyst to turn out more work with precision equal to or greater than that with the manual methods.

In conclusion it should be pointed out that D-5 is not against the use of new technology in the preparation of standards but, by the time the technology has been advanced and proven reliable, it is no longer new. To be considered worthy of standardization a new approach must be faster than the one it is to replace, must have equal or greater precision, and the equipment required must be within the reach of the laboratories who will be expected to use it.

Characterization of Liquids and Gases
Obtained by Hydrogenating Lumps of
Texas Lignite

C. V. Philip and Rayford G. Anthony

Department of Chemical Engineering
Texas A&M University
College Station, Texas 77843

INTRODUCTION

The increased cost of natural gas and the high cost of fuel oil have increased the importance of Texas lignite as a potential source of chemicals and as a fuel for generating electricity. The lignite resource in Texas has been estimated (1) as 10 billion tons at depths less than 200 feet and 100 billion tons at depths of 200 to 5000 feet. The shallow basin lignite can be recovered by strip mining but the deep basin lignite will probably have to be recovered by *in situ* mining methods. *In situ* liquefaction and comminution have considerable potential for recovering deep basin lignite (2,3,4).

In order to evaluate the potential of underground liquefaction, autoclave experiments have been conducted at pressures of 500 to 5000 psi and temperatures of 650 to 800°F. The charge to the autoclave has been cylinderical cores, 1 1/2 inch in diameter and 3 to 5 inches long, hydrogen, helium and hydrogen donor solvents. In order to gain insight into the reaction mechanisms underlying the conversion process, the liquid and gas products have been analyzed by use of several methods. Generally, coal-derived liquids have been characterized after separating different species by use of solvents with different chemical affinities (5,6). Since the composition of the lignite derived fluids are less complex compared to other coal-derived liquids, an analytical procedure based on boiling points of the components is used.

EXPERIMENTAL

Three Gow-Mac gas chromatographs, Model 69-550, with thermal conductivity detectors were used for simultaneous analysis of gases and liquids. The oven temperatures were manually programmed. Commercially available helium is used as carrier gas. Helium is purified by passing it through molecular seive 5A (3 ft. X 1 1/2" O.D. stainless steel column) and through a high capacity purifier (Supelco Carrier Gas Purifier) to remove the traces of oxygen and water. The gas chromatographs accept only 1/4" columns with a maximum length of 10 ft. Samples were injected directly into the column to avoid the recovery loss in the injection port. The products from lignite liquefaction experiments, which were analysed by gas chromatography can be classified as follows: (a.) gases; (b.) low boiling point liquids (boils below 100°C); (c.) high boiling point liquids (boils above 100°C).

Porapak N was used for identifying methane, carbon dioxide, ethylene, ethane, hydrogen sulfide, propane, water, isobutane and *n*-butane. After an initial 1 min. hold at 25°C, a shotgun temperature program – 25°C to 140°C at a rate of 15 to 20°C per min. – was used to get excellent separations. Molecular Sieve 5A could separate hydrogen, carbon monoxide, oxygen and nitrogen from the gas samples at room temperature. Porapak S also gave a separation similar to Porapak N but did not separate propane and water under identical conditions. The thermal stability of Porapak S (max. temp. 250°C vs. 190°C for Porapak N) favored it as a choice for a few samples.

The low boiling liquids were separated on two Durapak columns. Durapak *n*-octane on poracil C is good for separating aliphatic components while Durapak OPN on poracil C separates the aromatic compounds. The sample is run on both columns simultaneously under identical conditions. A shotgun temperature program from 25 to 150°C gave

fairly good separation of the components.

The high boiling point liquids contain nonvilatile components as well as lignite fragments which may deposit on the columns. The samples were cleaned to get the desired boiling point range by using a fractional sublimator. The sublimator consists of two concentric glass tubes. The outer tube holds the sample and the inner tube contains a coolant, like liquid nitrogen or dry ice-acetone mixture. The space between the tubes is evacuated while the outer tube is heated by a jacket type furnace. The temperature of the furnace is controlled by a Thermolyne proportional temperature controller. The sample temperature is recorded on a strip chart recorder. The sample evaporates and deposits on the outside of the inner tube (liquid nitrogen cold finger). The sample temperature and the degree of vacuum controls the volatility of the fractions deposited.

The clean samples from the sublimator were analysed using five different 8 ft. columns with packings that can withstand column temperatures well above 300°C without appreciable bleeding. The column temperature was programmed from 80°C to 280°C at a rate of 1.5 to 2°C per minute. The same sample was analysed with different columns under identical conditions. A hydrocarbon standard of n-alkanes ranging from C_{10} to C_{36} along with pristane and phytane was used to qualitatively identify the boiling point range of the components separated on different columns.

Detailed analysis of the lignite derived products were done on GC-MS. The apparatus mainly consists of a Hewlett-Packard 5710A Gas Chromatograph. A 5980A Mass Spectrometer, a 5947A Multi Ion Detector and a 5933A Data System. The gas chromatograph is able to accept packed columns as well as glass capillary columns. A 30 ft. X 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP and a 30 M glass capillary coated with OV 101 were used for most of the GC-MS studies. OV 101 is a methylsilicone polymer similar to the SP 2100 used in the Gow-Mac gas chromatographs. The hydrocarbon standard was used to determine the boiling point range of the components as well as the fragmentation pattern of the n-alkane series.

The proton nmr spectra of the samples dissolved in $CDCl_3$ were taken on a Varian T-60 nmr spectrometer. JEOL PS-100-PFT was used for scanning C^{13} nmr spectra of samples in $CDCl_3$. Samples used for these studies were not sublimated. The samples, therefore, contained high molecular weight species as well as minute suspended particles.

RESULTS AND DISCUSSION

The gaseous products from different lignite liquefaction experiments were composed of the same components but the composition varied depending on the experimental conditions and the lignite sample cores used. The gaseous components were identified using known standards and simple chemical tests. Figure 1 is a typical gas chromatogram for the gas sample obtained during the hydrogenation of wet Texas lignite. Carbon dioxide is the major component. Hydrogen sulfide is present in an appreciable concentration. Once both carbon dioxide and hydrogen sulfide were removed from the gaseous mixture, the product has a composition comparable to commercial natural gas containing a series of low molecular weight hydrocarbons with methane in large proportion.

Texas lignite is a low grade coal (8000 BTU per pound) with a high oxygen content (up to 30% of dry weight) and about a medium level of sulfur residues (nearly 2% of dry weight). Most of the carbon dioxide represents a major portion of the chemically bound oxygen in lignite which may exist as carboxylic groups. Hydrogen sulfide could be liberated from the sulfhydryl groups (thiols, sulfides, disulfides and chelated sulfur residues) and elemental sulfur (at least a small fraction) in the lignite.

The lignite-derived liquid obtained in this work is less complex than the bituminous coal-derived liquid. The lignite-derived liquid was divided into low boiling liquid and high boiling liquid in order to use two Durapak columns which have an upper temperature limit of about 150°C for the separation of aromatic and aliphatic compounds. As a matter of fact both the low and high boiling point liquids could be separated on any of the five columns used for high boiling liquid but the Durapak columns gave a much better resolution for the low boiling point liquid.

The low-boiling liquid is a clear colorless liquid which turns dark and cloudy on exposure to air at room temperature for a few hours. Figure 2 shows the total ion monitor chromatogram of the liquid using a 30 ft. 1/8" column packed with 3% OV 101 on Chromosorb W-AP. Table 1 summarizes the identification of major components and gives an overview of the general nature of the most common chemical species present in the low-boiling liquid. Aliphatic hydrocarbons, alkylated aromatics, furans and small amounts of thiophenes constitute the bulk of the sample. The mass spectra of these components clearly indicate the substance type, however, in cases where two or more hydrogen atoms have been substituted by alkyl groups, a large number of different patterns is possible. The mass spectra of some of these isomers are quite similar and so the identification has been done by using known standards or using individual boiling point range. All the possible isomers of some alkylated species are identified.

Table 1.   Identification of Major Components in the Low Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Acetone	19	Ethylbenzene
2	1,1-Dimethylcyclopropane	20	Xylenes
3	C_6H_{12}	21	2,3-Dimethylthiophene
4	Ethylmethylketone	22	C_9H_{20}
5	Hexane	23	2-Methyl 5-propylfuran
6	Methylcyclopentane	24	Cumene
7	1-Methylcyclopentene	25	$C_{10}H_{22}$
8	Pentane-2-one	26	t-Butylcyclohexanone
9	Heptene	27	p-Ethyltoluene +
10	2,4-Dimethylpentadiene		trimethylthiophene
11	Dimethylcyclopentene	28	Trimethylthiophene
12	Heptene	29	Trimethylthiophene (iso.)
13	C_7H_{12}	30	C_3-Alkylbenzene
14	Toluene	31	n-decane
15	2-Isopropylfuran	32	Tetramethylbenzene
16	C_8H_{12}	33	Cyclopropylbenzene
17	Isopropylfuran	34	Tetramethylthiophene
18	1-Ethylcyclohexene	35	C_4-Alkylthiophene
		36	$C_{11}H_{24}$

High boiling-point liquid was cleaned using a fractional sublimator prior to gas chromatographic analysis. The residue from sublimation was about 20 to 40% of the charge to the sublimator. The sample was sublimated to limit the boiling-point range of the sample so that the column temperature could be set for an upper limit of 280°C. Column bleeding was the major problem in GC-MS studies. Figure 3 shows the chromatogram of a sublimated sample and Table 2 list all the components identified. The same sample was separated on a Dexsil 300 GC column (Figure 4). Comparing the chromatogram of the same sample on five different column helps to resolve some components which may not separate on a particular column under identical conditions. For the GC-MS analysis a 30 ft. x 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP gave a better analysis than a 30M glass capillary column coated with OV 101 under similar conditions.

The Dexsil 300 GC column separated components into sharper symmetrical peaks in a shorter time compared to other columns. SP 2250 is the slowest of all. When a sample containing naphthalene and tetrahydronaphthalene is used on five different

33

columns, SP 2250 gave the best separation while SP 2100 gave no separation. The efficiency of separation in decreasing order can be listed as follows: SP 2250, Dexsil 410 GC, Dexsil 400 GC, Dexsil 300 GC and SP 2100. The bulk of the high-boiling-point liquid sample consists of saturated hydrocarbons mostly n-alkanes ranging from C_{10} to C_{36} distributed over the entire boiling point range. The aromatic species were predominantly alkylated phenols, benzenes, indenes, hydrogenated indenes and naphthalenes. Aromatic hydrocarbons containing three or more rings were not detected in the sublimated sample. The n-alkanes are not distributed proportionately throughout the series, though not a single member is missing. Unusually large enrichment occures at C_{10}, C_{17} and C_{27}. Mass spectral data of these higher members is not good enough to distinguish between a n-alkane and a slightly branched alkane of a higher molecular weight. The peak assigned to n-C_{17} alkane may also be assigned to branched alkanes with more than 17 carbon atoms, namely pristane, a branched C_{19} alkane. Pristane is derived from the phytol residues of chlorophyll (7). The hydrogenation products of other diterpene residues in lignite may also contribute to peaks in the range of C_{17} through C_{19}. The branched C_{30} alkanes obtained by the hydrogenation of triterpene type residues may be responsible for the n-C_{27} alkane peak enhancement.

Table 2. Identification of Major Components in the High Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Phenol	24	Pentamethylindan
2	1-Ethyl-3-methylbenzene plus Decane	25	C_6-Alkylindan
		26	Trimethylnaphthalene (iso.)
3	o-Cresol		
4	p-Cresol	27	$C_{16}H_{34}$ plus Trimethyl-nahthalene (iso.)
5	n-Undecane plus methylcresol		
6	o-Ethylphenol	28	n-Hexadecane
7	2,6-Dimethylphenol	29	Diethyl methylnaphthalene
8	p-Ethylphenol		
9	p-Cymene	30	$C_{17}H_{36}$ plus Tetra-methylnaphthalene
10	$C_{12}H_{26}$ plus 1,3-Dimethyl-indan	31	n-Heptadecane
11	n-Dodecane plus 2-Methyl-6-ethylphenol	32	Alkylated naphthalene
		33	$C_{18}H_{38}$
12	3-Methyl-6-ethylphenol	34	n-Octadecane
13	$C_{12}H_{16}$	35	$C_{19}H_{40}$
14	3-Methyl-6-ethylphenol	36	$C_{19}H_{40}$
15	$C_{13}H_{28}$ plus 1,6-Dimethylindan	37	$C_{19}H_{40}$
16	1,2-Dimethylindan	38	n-Nonadecane
17	n-Tridecane	39	n-Eicosane
18	$C_{11}H_{16}$(Methylated benzene)plus $C_{14}H_{30}$	40	n-Heneicosane
		41	n-Docosane
19	n-Tetradecane	42	n-Tricosane
20	Dimethylnaphthalene	43	n- Tetracosane
21	2,3-Dimethylnaphthalene	44	n-Pentacosane
22	$C_{15}H_{32}$	45	n-Hexacosane
23	n-Pentadecane	46	n-Hepacosane
		47	n-Octacosane

The high boiling liquid is composed of species with a very wide range of boiling points. Starting with phenol (181°C) at the low end and n-$C_{36}H_{74}$ (497°C) at the upper end. A careful examination of Table 2 reveals that fractional distillation or sublimation can be effectively used to separate the high boiling liquid into separate fractions enriched with phenols (180-230°C), aromatic hydrocarbons (230-300°C) and alkanes (300-500°C). Similarly the low boiling liquids can also be fractionated into

enriched samples. The minor components of the high and low boiling liquids are concentrated in these fractions and can be identified by use of GC and GC-MS.

The proton nmr spectra show the distribution of chemically bound hydrogen among the aromatic rings, aliphatic chains and other carbon atoms with varying chemical shifts due to different functional groups. The spectra give only a very qualitative picture about the chemical nature of the numerous components present in the lignite derived products. An approximate estimation of the aromatic and the aliphatic moieties in the sample could be attempted with reasonable success.

Due to the high resolution power of the C^{13} nmr spectroscopy a cumulative estimation of a sample containing many components may result in the disappearance of a large number of C^{13} absorptions in the noise. The sample spectra will show few nmr absorption peaks representing carbon centers with nearly identical chemical shifts. Each narrow peak is formed by summing up the nmr absorptions of C^{13} carbons from similar but different compounds. The C^{13} nmr spectra of a non sublimated high-boiling liquid derived from hydrogenated lignite has about ten major absorption peaks. These peaks are listed in Table 3. Three peaks are in the aromatic region (110-130 ppm) and seven in the aliphatic region (10-40 ppm). The peak at 14.19 ppm could be due to terminal methyl groups of saturated long chain hydrocarbons. The intense absorption at 29.91 ppm is due to methylene groups in the middle regions of one or more long chain saturated dydrocarbon compounds. Relatively very large area of the peak at 14.19 ppm suggests that n-alkanes are the bulk species in the lignite derived fluids. The C^{13} nmr studies also show that most of the GC peaks of alkanes are due to straight chain rather than branched hydrocarbons.

Table 3. C^{13} NMR Data of Products from Hydrogenated Lignite

Peak No.	Chemical Shift ppm	Peak Height(rel)	Peak Area(rel)
1	14.19	7.16	22.17
2	19.77	6.62	27.30
3	22.84	11.07	38.04
4	29.53	20.94	65.52
5	29.91	122.68	603.50
6	32.10	11.77	42.25
7	37.64	5.72	25.24
8	115.54	6.22	10.52
9	128.37	8.95	57.72
10	129.57	7.67	22.30

REFERENCES
1. W. R. Kaiser, "Texas Lignite: Near-Surface and Deep-Basin Resources" Report No. 79, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas (1974).
2. R. G. Anthony, Texas Engineering Experiment Bulletin No. 76-3, 4-13, (July, 1976).
3. D. R. Skidmore and C. J. Konya, Preprints Div. of Fuel Chem., ACS, Dallas (1973).
4. R. G. Aldrich, D. V. Keller, Jr. and R. G. Sawyer, U.S. Patent Nos. 3815,82 (July 11, 1974), 3850,477 (November 26, 1974), and 3870,237 (March 11, 1975).
5. J. E. Schiller, Hydrocarbon Processing, p. 147 (January, 1977).
6. W. Bertsch, E. Anderson and G. Holzer, J. Chromatography, 126 213-224 (1976).
7. J. M. Gilbert, I.M.R. DeAndrade Bruning, D. W. Nooner, and J. Oro, Chemical Geology 15, 209-215, (1975).
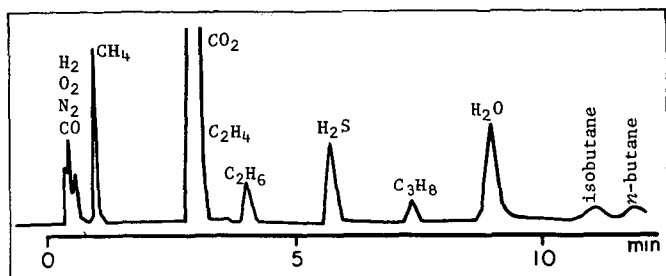
Fig. 1. Gas chromatogram of Texas lignite derived gas. Conditions: stainless steel column, 5ft x 1/4" O.D. packed with 80/100 Porapak N; carrier gas (helium) flow rate: 60 ml/min; temperature program: 25C (1 min.), 25-140°C at 15-20°/min.
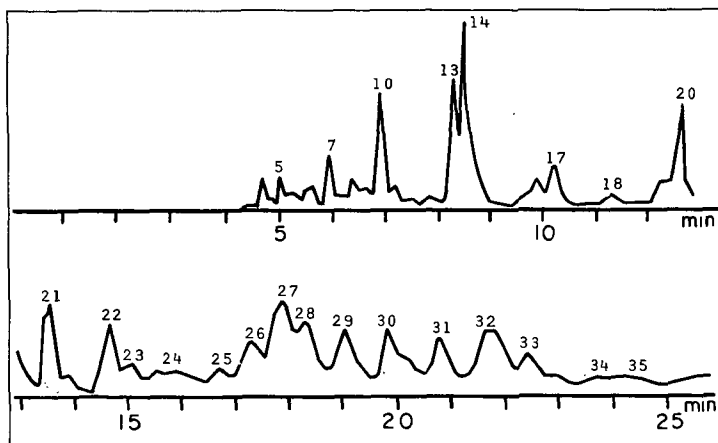
Fig. 2. Total ion current monitor chromatogram of low boiling liquid. Conditions: stainless steel column, 30ft x 1/8" O.D. packed with 3% OV 101 on 80/100 Chromosorb W-HP; carrier gas (helium flow rate: 20 ml/min; temperature program: 75-200°C at 2°/min. For identification of peaks see Table 1.

36

Fig. 3. Gas chromatogram of high boiling liquid. Conditions: stainless steel, 8ft x 1/4" O.D. packed with 10% SP 2100 on 100/120 supelcoport; carrier gas (helium) flow rate: 60 ml/min; temperature program: 100-250°C at 2/min. For identification of peaks see Table 2.
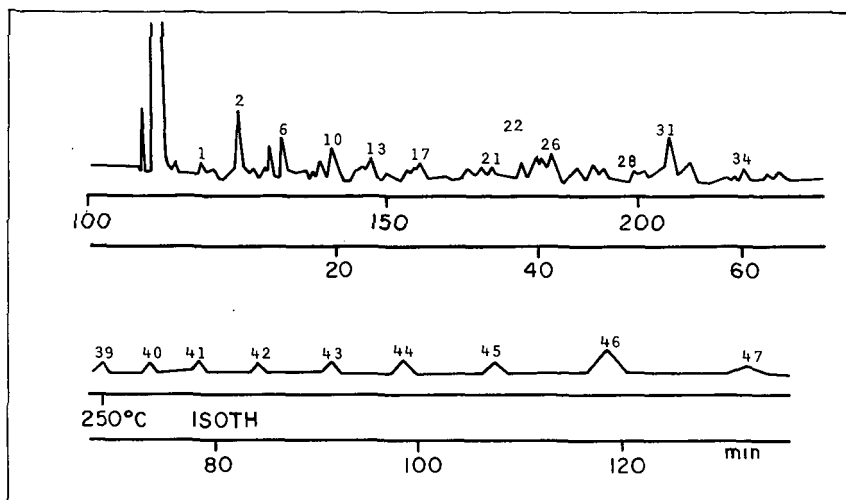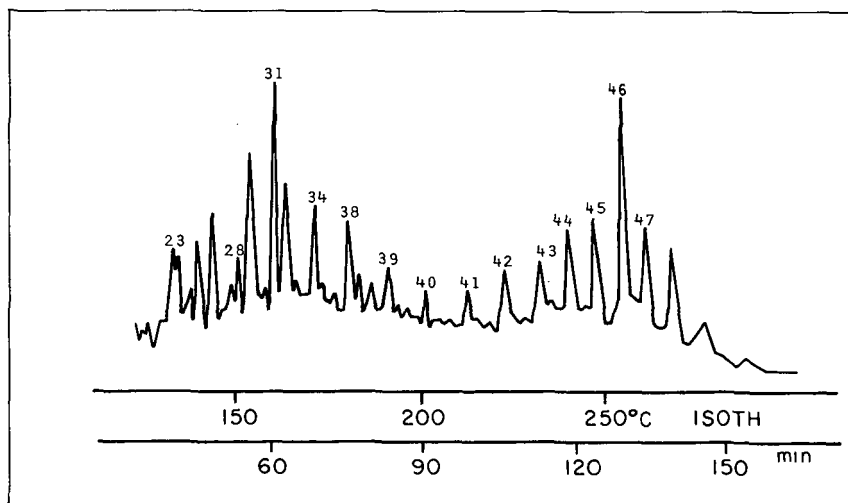

Fig. 4. High boiling liquid separated on a 3% Dexsil column. Column size and conditions are similar to those of Figure 3. For identification of peaks see Table 2.

37

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF
MODEL HYDROAROMATIC HYDROCARBONS AND SOLVENTS

Kalkunte S. Seshadri, Raffaele G. Ruberto,
Douglas M. Jewell, and Huey P. Malone

Gulf Science & Technology Company
P.O. Drawer 2038
Pittsburgh, PA 15230

INTRODUCTION

In recent years, a great deal of attention has been directed towards coal as an alternate source of gaseous and liquid fuels and chemicals which are currently derived from petroleum. Liquefaction of coal by catalytic hydrogenation was demonstrated by Bergius as early as 1912.[1] Subsequently other methods for coal liquefaction have been attempted and the kinetics of hydrogenation studied.[2] Coal can also be liquefied by hydrogen donor molecules, such as tetralin[3] and octahydrophenanthrene.[4] The initial reactions are thermal cleavage of carbon-carbon or carbon-oxygen bonds, resulting in free radicals. In the absence of hydrogen, free radicals polymerize producing high molecular weight solids. But if hydrogen donor molecules are present, the free radicals are stabilized resulting in low molecular weight liquids or gases. Tetralin is an efficient hydrogen donor molecule but many other structures can function in a similar manner.

Many coal liquefaction processes are currently in developmental stages – both catalytic and noncatalytic. These processes use coal-derived (anthracene oil) or petroleum-derived (decant oil) solvents. To enhance coal dissolution, they may be prehydrogenated or hydrogenated in-situ and the hydroaromatic hydrocarbons thereby formed partake in the formation of low molecular weight compounds from coal. An important aspect of coal liquefaction processes is therefore a basic understanding of the structure of the hydroaromatic molecules. Information is needed on the types that are present in aromatic solvents, the structures that are produced upon hydrogenation, their reactivity and the amount of "transferrable" hydrogen they may contain. The modus operandi that has succeeded in petroleum chemistry is separation of a complex mixture into simpler fractions, followed by their compositional analysis by spectroscopic techniques. The same method has been adopted here with promising results. The best spectroscopic technique capable of solving the problems posed above is carbon-13 NMR spectroscopy. However, because of the relative novelty of this technique, very little spectral information is available on hydroaromatic hydrocarbons and therefore a necessity arose to develop our own. This paper is a discussion of spectra and spectra-structure correlation of model hydroaromatic hydrocarbons, related compounds and fractions from partially hydrogenated condensed aromatic hydrocarbons.

RESULTS AND DISCUSSION

I   Spectral Assignments in Model Compounds

The numbering scheme and structures for the sixteen compounds studied are presented in Figure 1. Assignments of resonance positions were accomplished by several techniques. As a starting point for making the assignments, resonances of quaternary aromatic centers[5] were separated from those due to carbons directly bonded to hydrogens, by examining the off-resonance spectrum in which the former retain their singlet structure. Furthermore, there are differences in the relative

sensitivity and the shieldings between these two types of carbon atoms. Quaternary carbons, under normal instrumental conditions, do not attain the full nuclear Overhauser enhancement and therefore their resonances appear with reduced intensity and they are deshielded more than the protonated carbons. Also, empirical chemical shift additivity correlation and known information on model compounds were used in assigning values to a given carbon atom.

The results for tetralin (I) in $CDCl_3$ are in good agreement with those reported for neat tetralin,[6] but our values are about 1 ppm upfield from those in neat tetralin, probably due to solvent effect. The contribution of the phenyl group along an alkyl chain is to shift the shielding of the α-carbon by +23.0 ppm, the β-carbon by +9.5 ppm and the γ-carbon by ca. -2 ppm.[7] This information along with the results for tetralin is utilized in assigning values to carbon atoms in 2(ar)-butyltetralin (II). The contribution of the aromatic ring of this molecule along the butyl chain is almost identical to that observed in n-butylbenzene. The effect of the chain on the saturated ring is marginal. The shieldings of C-6 and C-7 are unchanged, but a doublet, differing by 0.4 ppm in chemical shift, is observed around 29 ppm. An upfield shift of 0.4 ppm is similar in magnitude to the δ-effect observed in substituted cyclohexanes.[8] Therefore the line at 29.1 ppm is assigned to C-8 and the line at 29.5 ppm to C-5. Naturally, more pronounced effects have to be expected on the shieldings of aromatic carbon atoms. It is evident from the reduced NOE that resonances at 139.8, 136.6 and 134.1 ppm are due to three quaternary centers in the molecule. Butyl substitution decreases the C-2 shielding by +14.0 ppm and increases the C-4a shielding by -3.0 ppm. The latter is the familiar "para" effect. So C-2 is given the value 139.8 ppm and C-4a 134.1 ppm. The rest of the assignments are in Table I.

Assignment of values to carbons in 2(ar)-n-butyl-8-n-hexyl tetralin (III) is attempted, considering (I) and (II) as models. The contribution of a cyclohexyl ring along an alkyl chain can be derived from the results published by Adams and Lindeman[9] and are similar but not identical to those of a phenyl ring; α-carbon is deshielded by ca. +24 ppm, β-carbon by ca. +4 ppm, and the γ-carbon is shielded by -2 ppm, compared to the parent alkane. The contribution of the hexyl-chain to the ring carbons can be ascertained from the results on saturate hydrocarbons[9] and alkyl benzenes.[7] C-8a, due to the hexyl group on C-8, experiences a deshielding β-effect and a shielding γ-effect. These combined effects would place its chemical shift 4 ppm downfield from the corresponding value in tetralin or butyltetralin and so the value 141.2 ppm is assigned to C-8a. There appears to be γ-effect on C-1, similar in magnitude to that observed, for example, in n-butylbenzene: an upfield shift of 0.5 ppm. C-2, C-3, C-4 and C-4a are unperturbed. A normal alkyl chain, longer than C_4, decreases the shielding of substituted carbon by ca. +9 ppm and so one of the lines around 37 ppm is due to C-8. β-effect of lesser magnitude would place the resonance of C-7 around 27 ppm. C-5 is least perturbed and so its chemical shift value would be 29.5 ppm. Recalling the α, β, and γ effects of a cyclohexyl ring along the alkyl chain and remembering that the chain is n-hexyl, the chemical shift values to be expected for α, β, and γ carbons to the ring in the hexyl chain are respectively about 37, 27, and 29 ppm. This mutual interaction has resulted in three pairs of closely spaced lines and sorting them out is indeed a problem. The chemical shift value of C-5 in (II) and (III) can be expected to be identical. So the value 29.5 ppm is assigned to C-5 and 29.7 to C-8γ. In the off-resonance experiment the line at 37.2 is split into doublet, while the line at 37.7 into a triplet. So the former is assigned to C-8 and the latter to C-8α. The distinction that has been made between C-7 and C-8β is arbitrary. We have so far accounted for all the lines except the one at 20.1 ppm, which has to be associated with C-6. The upfield dis-

placement of C-6 (3.5 ppm) relative to that observed in (II) indicates a γ relation-
ship between the hexyl chain and C-6. All the four carbon atoms in the saturated
ring of tetralin are not coplanar with the aromatic ring. A 'half-chair' and 'half-
boat' conformations are possible.[10] We think that the carbon atoms 6 and 7 are
above the plane of the aromatic ring and consequently C-6 experiences an upfield γ
steric shift.[8]

Chemical shift values for carbons in three gem substituted tetralins are
given in Table I. The assignment of chemical shift values in 8,8-dimethyltetralin is
facilitated by careful intensity measurement and the decoupling characteristics of
signals. There are two interesting changes relative to tetralin; 16.2 and 4.3 ppm
downfield shifts of C-7 and C-8, respectively, which is analogous to the shifts
observed in 1,1-dimethylcyclohexane.[11] In 8,8-diethyltetralin (V), C-8 is further
deshielded while the effect of ethyl substitution is the upfield displacement of C-7.
Downfield displacement of C-8 is due to β-effect while the upfield displacement of C-
7 is due to 'γ' relationship between the methyl carbon of ethyl group and the C-7
position. This trend is noticed in the transition from methylcyclohexane to ethyl-
cyclohexane.[9] In 8,8-dibutyltetralin (VI), the shielding of C-8 is slightly in-
creased, while curiously enough, the shielding of C-7 is decreased by +1.3 ppm. We
have not understood these effects. The other changes are qualitatively similar to
those observed in substituted cyclohexanes.[8,11]

Results for 9,10-dihydrophenanthrene (VII) and sym-octahydrophenanthrene
(VIII) in CDCl$_3$ are similar to those reported by Retcofsky and Friedel[6] in neat
liquid. But C-1, C-2 and C-3 in (VII) and C-4a and C-10a in (VIII) are not identical
as suggested by their results. The carbon chemical shifts in (I) and (VIII) have
been calculated by them by considering these structures as being benzene ring in
which pairs of adjacent hydrogens are progressively replaced with six-membered
hydroaromatic rings and equating them to appropriate multi-methyl substituted ben-
zene. This scheme has provided values for the chemical shifts of aromatic carbons,
agreeing well with the observed results. It remains to be seen whether this method
is applicable to other molecules considered here. For example, is it possible to
predict the shielding of aromatic carbons in 1,2,3,4-tetrahydrophenanthrene knowing
the values for carbons in 1,2-dimethylnaphthalene? Several dimethylnaphthalenes have
been studied by carbon NMR,[12] but no detailed information is yet available on 1,2-
dimethylnaphthalene. Spectral information on a variety of multi-methyl substituted
naphthalenes may facilitate assignment of values to carbons in partially hydrogenated
pyrenes also. In the absence of such information, assignment of chemical shifts to
appropriate carbon atoms in structures (VII) to (XVI) is accomplished by comparing
the results with those of parent aromatic compound, among themselves and by other
considerations.

In (X), the shieldings of carbons in positions 4b, 5, 6, 7 and 8 should be
comparable to those in the corresponding positions of phenanthrene. So the lines at
122.7, 125.5, 125.6, 128.1 and 131.2 are associated respectively with C-5, C-6, C-7,
C-8 and C-4b. To select values for other carbons, the molecule is considered as
perturbed phenanthrene. The effect of saturated carbons is most pronounced at
positions 10, 4a and 10a. A deshielding of +1.5 ppm is reasonable for C-10 and so
the line at 128.3 ppm is assigned to it. The shieldings of C-4a and C-10a are
expected to decrease by about +2 ppm and they are assigned the values 132.7 and 133.9
ppm, respectively. These assignments leave us with two lines, one at 132.2 ppm and
the other at 124.5 ppm. For obvious reasons, the former has to associate with C-8a
and by the process of elimination, the latter with C-9. C-9 is shielded due to the
para effect, which raises the question why C-8a is not experiencing a similar para

effect. An examination of chemical shift of carbons in 1-methylnaphthalene (1-MN) and 2-methylnaphthalene (2-MN), relative to naphthalene[12] provides a satisfactory answer, although qualitative. C-4 experiences a shielding para effect in 1-MN, while it is deshielded in 2-MN. C-4a experiences similar effects, but the magnitudes of these effects are not identical at these two centers. The combined effect of methyl substitutions at positions 1 and 2 is an upfield shift at C-4 and no change at C-4a. C-4 and C-4a in 12-DMN corresponds to C-9 and C-8a respectively in (X). The calculation of chemical shift values for carbons in 12-DMN, starting from 1-MN and 2-MN, although unorthodox without the knowledge of steric effect due to substitutions ortho to each other, has provided some information on the shieldings of C-9 and C-8a due to hydrogenation of one of the terminal rings in phenanthrene. Our assignments are further substantiated by the spectrum of octahydrophenanthrene (VIII) relative to 1,2,3,4-tetrahydrophenanthrene. The spectrum of VIII has three lines of equal intensity in the region where aromatic carbons absorb. The line at the lowest field is assigned to C-8a and C-10a and the line at 134.0 ppm to C-4a and C-4b. The combined effect of two saturate rings on the quaternary carbons results in the merging of lines due to C-4a and C-4b to a singlet, with a similar effect on C-10a and C-8a. The effect of a saturated ring on C-10 in (X) is a decrease in shielding by +1.4 ppm and on C-9, an increase in shielding by -2.4 ppm, compared to phenanthrene. C-9 and C-10 are subjected to similar changes by the other saturated ring in (VIII). C-10 is shielded by about the same magnitude and the shielding of C-9 is decreased by +2.0 ppm. The combined effect of increase and decrease in shielding, due to the successive hydrogenation of the outer two rings in phenanthrene, results in the same resonance frequency for C-9 and C-10.

The next interesting pair of compounds in the phenanthrene class are 9,10-dihydrophenanthrene (VII) and its dimethyl derivative (IX). As observed in other molecules in this class, para shielding effect is evident in (IX). But more interesting, this molecule constitutes another example of the recently reported deshielding 'δ' effect, where substantial downfield shifts are found in compounds containing spatially interacting δ function.[13] In the two partially hydrogenated phenanthrene molecules that we have so far examined, assignment of values to quaternary centers was accomplished by the procedure mentioned earlier, and by using the results on phenanthrene published by Ozubko and co-workers.[14] In (IX), methyl substitution in strategic positions provided an additional handle in selecting values to quaternary carbons. The spectrum of (IX) has three lines with reduced intensity at 141.3, 135.1 and 134.7 ppm, of which the last one is the least intense. Quaternary carbons in position 5 (4) and 8a (10a) have protons in ortho positions, while that in position 4a (4b) is devoid of protons in its immediate vicinity. It is reasonable to expect that relaxation is determined by the $^{13}C-^1H$ dipole-dipole mechanism and consequently, C-4a should have the longest relaxation time (T_1). Based on this consideration, the line at 134.7 ppm is assigned to C-4a (C-4b). Substantial downfield shift (6.6 ppm) due to 'δ' shielding effect is observed for C-1 in 7,12-dimethylbenz[a]anthracene compared to 7-methylbenz[a]anthracene.[14] A larger downfield shift for C-5 (4) is possible due to mutual 'δ' effect added to the downfield shift due to methyl substitution, compared to C-5 in (VII). So the line at 141.3 ppm is assigned to C-5 (4) and the remaining line at 135.1 ppm to C-8a (10a). The difference in the relaxation times (T_1) between C-4a (4b) and C-8a (10a) surfaced in this molecule due to -CH$_3$ substitution at C-4 (5), and permitted an unambiguous assignment to quaernary centers, and has also helped us to understand the spectrum of (VII) and other lines in the spectrum of (IX). Carbon chemical shifts in tetralin follow the trend in o-xylene.[6] So it is reasonable to expect the trend in 9,10-dihydrophenanthrene to be similar to that in 2,2'-dimethylbiphenyl. But no spectral information is available on the latter. Nevertheless, approximate values for the chemical shifts of quarternary

carbons can be calculated from the chemical shift values of carbons in biphenyl.[15] This calculation indicates that the resonance of C-4a (4b) in (VII) should be at a lower field than that of C-8a (10a). Upon -CH$_3$ substitution in positions 4 and 5, the changes that can be expected are the shieldings of C-8a and C-10a to be practically the same, while those of C-4a and C-4b to be increased by about -2.5 ppm. The latter is a manifestation of γ steric effect. These changes are indeed observed, substantiating the assignment of values to C-8a (10a) and C-4a (4b) in (IX). There are four lines, three of which are closely spaced, in the spectrum of VII corresponding to four protonated aromatic carbons. Methyl substitution separates the three closely spaced lines and the separations have been useful in arriving at further assignments. Methyl substitution decreases the shielding of C-6 and increases that of C-8, leaving the value of C-7 unchanged. The para shielding effect -2.4 ppm is similar in magnitude to that observed in other aromatic structures. The complete assignments are in Table II, along with those for the saturated carbons.

The next class of compounds which have been investigated are pyrenes and partially hydrogenated pyrenes. The spectrum of 3-n-decylpyrene (XI) is included, although it is not a hydroaromatic, to understand the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene, and also to assess the contribution of a multi-nuclear aromatic structure along an alkyl chain. Shieldings at carbons 1,5,6,7,8,9,10,13 and 14 are similar to those for the corresponding carbons of pyrene (XVI). Amidst the group of lines corresponding to aromatic carbons directly bonded to protons, there is a line at 125.0 ppm with reduced intensity, which has to be associated with quaternary centers and we think that it corresponds to the line at 124.5 ppm in the spectrum of pyrene, which is assigned to C-15 and C-16.[16] The theory predicts that C-15 and C-16 should have similar chemical shift to other bridgehead positions. It is reasonable to explain both of these upfield shifts with an anisotropic ring current in the peripheral ring carbons. The line at the lowest field, 137.1 ppm, is assigned to C-3. The shielding of C-2 is likely to be slightly decreased and so the line at 126.3 ppm is assigned to it. The upfield shift of 3.9 ppm at C-4, relative to pyrene is again attributed to a γ steric shift. The remaining two lines are at 128.5 and 129.6 ppm. The shielding of C-11 is expected to increase by about -2.5 ppm due to para effect, and so the line at 128.5 ppm is assigned to it. By default the line at 129.6 ppm is assigned to C-12.

We have sufficient evidence, considered later, to believe that the di-plus triaromatic fraction of hydrogenated pyrene contains symmetric hexahydro and tetrahydropyrenes. Symmetric tetrahydropyrene in pure form has been studied by us and by subtraction, the chemical shift values for carbons in symmetric hexahydropyrene have been obtained. This information is utilized in understanding the spectrum of 4-n-decyl-1,2,3,6,7,8-hexahydropyrene (XII). In (XV) the chemical shift value for the carbons at positions 4,5,9,10 is 123.4 ppm. Alkyl substitution at C-4 has least effect on C-9 and C-10, and so they are assigned the values 123.5 and 122.5 ppm, respectively. The other line which we believe is due to a protonated aromatic carbon is at 126.1 and is associated with C-5. The shielding is decreased more than expected. Again, the line at the lowest field is assigned to C-4. The anisotropic ring current effect should be less pronounced in this compound compared to pyrene; consequently, the shielding of C-15 and C-16 is expected to be comparable to other bridgehead carbons. However, the NOE is less at these two centers compared to positions 11, 12, 13 and 14. The assignments are given in Table III.

The assignment of values to saturate side-chain and ring carbons is less complicated. The values for the side-chain carbons are given in Table IV, while those for ring carbons are included in Table III. Shifts for side-chain carbons in

42

(XI) and (XII) should be close and by comparing the spectrum of these two compounds upfield from 35 ppm, the lines due to hydroaromatic carbons are selected and their shielding should be comparable to corresponding carbons in symmetric hexahydropyrene, except for C-3. γ steric shift, observed in other structures, increases its shielding. The chemical shift values for carbons in symmetric tetrahydropyrene are given in Table III. The other compound that we have studied in this class is 1,2,3,9,10,11-hexahydropyrene and its values are also given in Table III.

II   Compositional Analysis of Fractions
From Hydrogenated Condensed Aromatics

In our studies on induced dissolution of coal by hydrogen donor solvents, several solvents in bulk quantities were prepared. They can be divided into two classes. One, resulting from the hydrogenation of fairly pure aromatic compounds and the second, from the hydrogenation of coal and petroleum-derived oils. The major effort in this study was the separation of the solvent and the reaction products into[17] mono- and di-plus triaromatic fractions and the examination of the fractions by different spectroscopic techniques to understand the reaction mechanism. Carbon-13 spectra of some of the fractions from the hydrogenated phenanthrene and pyrene model solvents are considered here. The composition of the fractions, even after separation, is extremely complex due to unconverted parent aromatic compound or compounds and numerous products resulting from cracking. However, the major contributions to the intensities in the saturate region are from hydroaromatic hydrocarbons, facilitating their recognition in the mixture. The analysis of real solvents is underway and will be discussed in a future publication.

The simplest system is di-plus triaromatic fraction of hydrogenated pyrene. In the region where saturated carbons absorb, three lines are observed at 31.4, 28.3, and 23.3 ppm. Resonance line positions of aromatic carbons are at 135.3, 134.0, 130.6, 130.1, 127.0, 125.9, and 123.4 ppm. From our previous experience, it is obvious that the line at 28.3 ppm is due to the four equivalent saturated carbons of tetrahydropyrene and the other lines associated with this structure are in the spectrum. The line at 31.4 ppm is twice as intense as the line at 23.3 and the one at 123.4 ppm, which does not belong to symmetric tetrahydropyrene, splits into a doublet in the off-resonance experiment. These observations suggest that these three lines in the spectrum are due to symmetric hexahydropyrene and the resonance lines due to quaternary centers are at 134.0 and 130.1 ppm. The structure of this compound is included in Figure 1 and complete assignments in Table III. There is no evidence for the presence of unsymmetric hexahydropyrene, which can be recognized because of bridgehead saturated carbons in the structure. The spectrum of di-plus triaromatic fraction of hydrogenated phenanthrene is also complex. However, if weak lines are ignored and only intense lines are considered, they account for two structures: 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene. The spectrum of the mono-aromatic fraction also has several lines, but intense lines are due to symmetric octahydrophenanthrene. The major hydroaromatic hydrocarbons that are formed on hydrogenation of phenanthrene are 9,10-dihydro-, 1,2,3,4-tetrahydro- and symmetric octahydro-derivatives. But unlike in the case of pyrene, a large number of other products are formed, some of which are due to ring openings.

It is accepted that the induced dissolution of coal is by hydrogen transfer from hydroaromatic hydrocarbons and so an effort was made to understand the carbon-13 spectra of model compounds and solvents. In a large scale process, it would be prohibitively expensive to use pure compounds or model solvents as a source of hydrogen. Hydrogenated coal and/or petroleum-derived solvents are attractive

substitutes. We are examining by carbon-13 NMR hydrogenated anthracene and decant oils and have identified several hydroaromatic structures in them. However, to understand the kinetics of hydrogen transfer reaction and thereby further improve the coal solvation process, the results have to be quantified. The cliche that carbon-13 NMR spectroscopy is analytically difficult is no longer true. Work is in progress in our laboratory to overcome some of the problems inherent to quantitative carbon NMR and initial results are gratifying. The composition of hydrogenated and unhydrog-enated real solvents, quantification of results will be the subject of future reports.

<center>EXPERIMENTAL</center>

Materials

        Compounds I and VII were obtained from Aldrich Chemical Company, Inc. and compound XIII from K and K Laboratories, Inc. Compound X is an API reference mater-ial. Compounds IV, V and VIII were specially prepared for us by Oklahoma State University. The rest were drawn from the hydrocarbon bank of Pennsylvania State University. All compounds and solvents were used without purification.

Spectra

        Nuclear magnetic resonance spectra of ^{13}C in natural abundance were obtained by the pulsed FT technique at 20 MHz on a Varian CFT-20 spectrometer, which is equip-ped with 620/L computer with 16K memory. The free induction decays, after a suf-ficient number of transients have been accumulated, were smoothed with an exponential function and Fourier transformed. Samples were studied in 8 mm OD tubes at a concen-tration corresponding to about 200 mg in a total volume of 1.4 ml and at a probe temperature of 36°C. The solvent was invariably $CDCl_3$. The deuterated solvent was used as a field-frequency lock and chemical shifts are in ppm downfield from internal TMS. The initial spectrum in each case was obtained with proton noise decoupling; later as the situation demanded, off-resonance decoupling and suppressed NOE spectra were obtained to facilitate spectral assignment.

<center>44</center>

REFERENCES

1. Bergius, F., _J. Gasheleucht_, 54 748 (1912).

2. Hill, G. R., Anderson, L. L., Wiser, W. H., Qader, S. A., Wood, R. E., and Bodily, D. M., Final Report to Office of Coal Research, Project Western Coal: Conversion of Coal to Liquids, University of Utah, May 1970.

3. Curran, G. P., Struck, R. T. and Gavin, E., _Ind. Eng. Chem. Proc. Design and Dev._, 6, 166 (1967).

4. Ruberto, R. G., Cronauer, D. C., Jewell, D. M., Seshadri, K. S., _Fuel_, 56, 17 (1977).

5. Quaternary carbons in a structure are those with no hydrogen atoms attached to them.

6. Retcofsky, H. L. and Friedel, R. A., in "Spectrometry of Fuels," (R. A. Friedel, Ed.), p. 90, Plenum Press, New York, 1970.

7. Stothers, J. B., "Carbon-13 NMR Spectroscopy," pp 97-98, Academic Press, New York, 1972.

8. Dalling, D. K. and Grant, D. M., _J. Amer. Chem. Soc._, 94,5318 (1972).

9. Adams, J. Q. and Lindeman, L. P., PREPRINTS, Div. of Petrol. Chem., ACS, 17 (2), C-4 (1972).

10. Hanack, M., "Conformation Theory," p. 207-208, Academic Press, New York, 1965.

11. Dalling, D. K. and Grant, D. M., _J. Amer. Chem. Soc_, 89,6612 (1967).

12. Doddrell, D. and Wells, P.R., J. Chem. Soc. Perkin II, 1333 (1973).

13. Buchanan, G. W., Stothers, J. B., and Wood, G., _Can. J. Chem_, 51,3746 (1973).

14. Ozubko, R. S., Buchanan, G. W. and Smith, I. C. P., _Can. J. Chem._, 52,2493 (1974).

15. Schulman, E. M., Christensen, K. A., Grant, D. M. and Walling, C., _J. Org. Chem._, 39,2686 (1974).

16. Alger, T. D., Grant, D. M. and Paul, E. G., _J. Amer. Chem. Soc._, 88,(5397), 1966.

17. Ruberto, R. G., Jewell, D. M., Jensen, R. K., Cronauer, D. C., _Advances in Chemistry Series_ 151,28 (1976).

Table I

<u>13C SHIELDINGS FOR RING AND SIDE CHAIN CARBONS IN I-VI (δ^C FROM TMS)</u>

	Compound					
Position	I	II	III	IV	V	VI
C-1	129.0	129.0	128.5	126.5	127.0	126.8
C-2	125.4	139.8	139.7	126.0	125.5	125.6
C-3	125.4	125.7	125.6	125.3	125.0	125.0
C-4	129.1	129.0	128.8	129.1	129.0	129.0
C-4a	136.9	134.1	134.0	135.6	137.8	137.4
C-5	29.4	29.5	29.5	30.9	30.8	30.9
C-6	23.4	23.6	20.1	20.0	19.8	20.0
C-7	23.4	23.6	27.6	39.6	30.8	32.1
C-8	29.4	29.1	37.2	33.7	40.1	39.8
C-8a	136.9	136.6	141.2	145.3	143.3	143.9
C-2α		35.4	35.5			
C-2β		34.0	34.0			
C-2γ		22.6	22.5			
C-2δ		14.0	14.0			
C-8α			37.7	31.9	34.4	42.7
C-8β			27.7		8.7	26.6
C-8γ			29.7			23.7
C-8δ			32.1			14.1
C-8ε			22.8			
C-8ζ			14.1			

Table II

<u>13C SHIELDINGS FOR RING AND $-CH_3$ CARBONS IN VII-X (δ^C FROM TMS)</u>

	Compound			
Position	VII	VIII	IX	X
C-1	127.2	30.2	124.3	30.3
C-2	126.8	23.8	126.4	23.2
C-3	128.0	23.2	129.0	22.9
C-4	123.6	26.3	141.3	25.5
C-4a	137.1	134.0	134.7	132.7
C-4b	137.1	134.0	134.7	131.2
C-5	123.6	26.3	141.3	122.7
C-6	128.0	23.2	129.0	125.5
C-7	126.8	23.8	126.4	125.6
C-8	127.2	30.2	124.3	128.1
C-8a	134.4	134.8	135.1	132.2
C-9	28.9	126.5	31.5	124.4
C-10	28.9	126.5	31.5	128.3
C-10a	134.4	134.8	135.1	133.9
C-4α			20.6	
C-5α			20.6	

46

Table III

^{13}C SHIELDINGS FOR RING CARBONS IN XI–XVI (δ^C FROM TMS)

Position	Compound					
	XI	XII	XIII	XIV	XV	XVI
C-1	124.5	30.9	125.8	30.9	31.4	124.8
C-2	126.3	23.2	126.9	22.8	23.3	125.7
C-3	137.1	27.4	125.8	31.1	31.4	124.8
C-4	123.3	135.6	28.2	127.5	123.4	127.2
C-5	127.4	126.1	28.2	124.2	123.4	127.2
C-6	124.6	31.5	125.8	124.3	31.4	124.8
C-7	125.5	23.3	126.9	125.6	23.3	125.7
C-8	124.6	31.5	125.8	125.5	31.4	124.8
C-9	127.0	123.5	28.2	29.9	123.4	127.2
C-10	127.0	122.5	28.2	30.6	123.4	127.2
C-11	128.5	133.5	135.2	37.6	134.0	131.0
C-12	129.6	130.3	135.2	136.0	134.0	131.0
C-13	131.4	133.9	135.2	134.3	134.0	131.0
C-14	130.9	133.8	135.2	131.3	134.0	131.0
C-15	125.0	130.5	130.4	132.2	130.1	124.5
C-16	125.0	129.0	130.4	129.6	130.1	124.5

Table IV

^{13}C SHIELDINGS FOR SIDE CHAIN CARBONS IN XI AND XII
(^{C} FROM TMS)

Position	Compound	
	XI	XII
CC-1*	33.5	33.4
CC-2	31.8	31.5
CC-3	29.8	29.9
CC-4	29.6	29.7
CC-5	29.6	29.7
CC-6	29.6	29.7
CC-7	29.3	29.4
CC-8	31.9	31.9
CC-9	22.7	22.7
CC-10	14.1	14.1

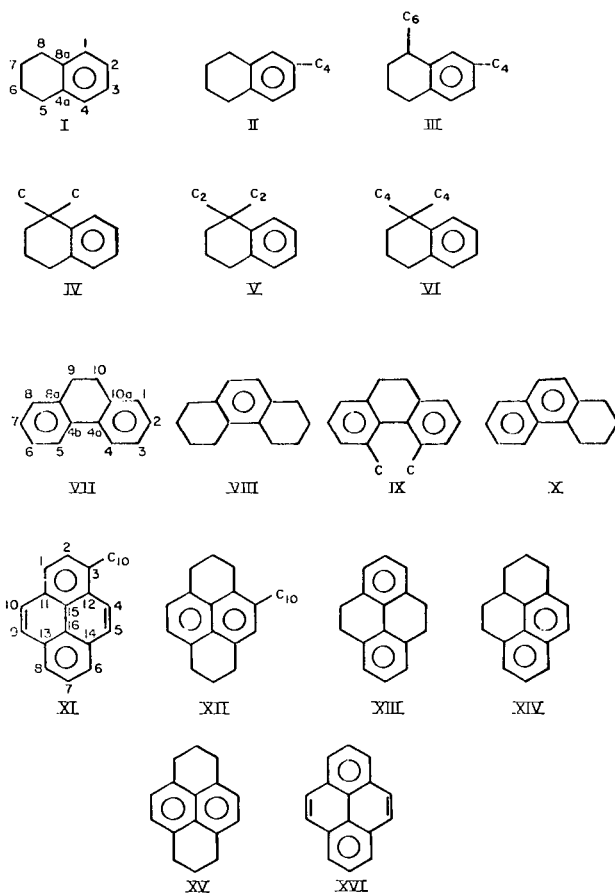
*CC-1 is the first carbon α to the ring.

47

FIGURE I: NUMBERING SCHEME FOR HYDROAROMATIC HYDROCARBONS

Multielemental Analysis Using Proton Induced Photon Emission

P. C. Simms, F. A. Rickey, and K. A. Mueller

Department of Physics, Purdue University, W. Lafayette, Indiana 47907

Energetic protons from a nuclear accelerator can be used to provide quantitative analysis for most elements from Li to Pu. The sample is prepared as a thin film and bombarded with protons to produce monoenergetic x rays and γ rays from all elements in the sample. Energy sensitive Si-Li and Ge-Li semiconductor devices are used to detect x rays and γ rays, respectively. The energy of the radiation identifies the element and the intensity determines the concentration of the element in the sample. A PDP 15/45 on-line computer is used to process data from one sample while data is being accumulated from the next sample. The analysis results are available from the computer at approximately the same time that new data accumulation is finished.

Proton excitation provides better sensitivity than electron excitation because the yield of characteristic x rays compared to background radiation is higher. Protons have an advantage over x-ray excitation because good sensitivity can be obtained for a much larger group of elements in a single measurement. In addition, the light elements Li, B, F, Na, Mg, Al, and Si can be detected by γ-ray emission following nuclear excitation.

The broad elemental range of Proton Induced X-ray Emission (PIXE) occurs because the production of characteristic x rays is very large in the energy region where the background radiation is maximum. The primary source of background radiation comes from showers of electrons which are released when a proton strikes the target. These electrons stop in the target and produce a continuous x-ray spectrum called Bremmstrahlung or braking radiation. The Bremsstrahlung intensity decreases rapidly as a function of energy and is essentially negligible above 10 keV for 4 MeV incident protons. The background at higher energy is primarily due to nuclear γ rays which occasionally interact with the x-ray detector. The probability for K x-ray emission also decreases with the atomic number of the element, but the x ray yield is still satisfactory up to the rare-earth elements because the background is so small. Elements heavier than La are detected by L x rays. The L x-ray yields for the rare-earths are good but their energy falls in the region of relatively high Bremsstrahlung so the sensitivity is poorer than for other regions. For heavier elements the L x rays occur above the Bremsstrahlung so the sensitivity is again excellent. The background in the γ-ray detector depends on the major components in the sample. For example, large quantities of Na or Cu in the sample can produce relatively intense γ-ray background.

Sample preparation. Solid samples are usually ground to a fine powder using Agate components in a vibrating mill or a mortar and pestle. A few milligrams of the fine powder is placed on a thin plastic film (2.5×10^{-3} mm thick) and weighed with a micro-balance. A few drops of liquid plastic are added and the sample is stirred with a plastic rod to make a uniform suspension of the fine powder. When the plastic solvent evaporates, the sample is firmly attached to the backing in a light weight matrix. The sample uniformly covers a 16 mm diameter circle. The plastic film with sample is mounted in a 35 mm photography slide frame. The sample is not damaged in the bombardment so it can also be studied with other techniques. Thin samples are preferable to minimize x-ray absorption and to avoid corrections due to slowing down of the protons in the sample. However, thick solid samples can be analyzed with slightly poorer sensitivity and accuracy. Materials desolved in an aqueous sample can also be deposited on thin films for analysis.

Target bombardment chamber. The proton beam passes through a 2.5×10^{-3} mm Al foil located 3 meters in front of the target to diffuse the beam and ensure that

the proton bombardment is uniform over the target area. The beam is restricted
with a series of collimators to ensure that the protons can only strike the sample
and the thin support film. Carbon or plastic films are used to cover all metal
parts of the chamber that might be struck by protons scattered from or passing
through the target. Bombardments are performed in vacuum. Eighty targets are held
in the circular slide tray of a modified 35 mm slide projector. The target to be
bombarded is dropped into the proton beam by the automatic mechanism of the
projector. A variety of filters can be inserted between the target and the
detector by remote control to reduce the intensity of abundant x rays which would
interfere with the analysis of trace elements. The x rays pass through a 0.025 mm
plastic window on the target chamber and a 0.025 mm Be window on the detector
cryostat.

   Detector and electronics. A Si-Li detector (1 cm diameter and 3 mm thick)
provides 170 eV energy resolution for 5.9 keV x rays. A 40 cm^3 Ge-Li detector
provides 2.0 keV resolution for 1.33 MeV γ rays. Normally when an x ray is
absorbed in the detector, all of the x-ray energy is converted into an electrical
pulse. However it is also possible for a Si x ray, created in the detection
process, to escape from the detector. These "silicon escape" events create false
peaks in the x-ray spectrum. It is also possible for electrons released in the
detector process to leave the surface of the detector. These events produce a
small tail on the low energy side of peaks in the x-ray spectrum. The computer
must be able to correct for these two imperfections in the detector response in
order to get accurate analytical results.

   The electrical signal from the detector is amplified and passed through a
noise filter which is essential for good energy resolution. Fifty microseconds are
required for the noise filter to process each x ray pulse. If a second x ray is
detected while the filter still contains a preceding x ray, the energy of both x
rays is distorted. This problem is greatly reduced in our system by switching the
proton beam off of the target shortly after the first x ray is detected. As soon
as the noise filter has processed the x ray pulse, the beam is automatically
returned to the target to produce a new x ray.

   Even though the beam switching time is less than 0.5 μsec, there is still a
small probability that a second x ray will be produced before the beam is removed
from the target. When two x ray pulses pile up in the filter a single pulse is
produced which corresponds to the sum of the energy of the two x rays. We have
developed a circuit which recognizes pile-up events and rejects them unless the
second x ray is emitted within 0.05 μsec of the first x ray. These remaining
"simultaneous" pile-up events are rare, so they usually do not present a signifi-
cant limit on the analysis.

   The task of separating events which come from two x rays of similar energy
is greatly simplified if the energy calibration of the electronic system is very
stable. The energy calibration is always a function of the counting rate in the
detector. Our system has correction circuits (Kevex Model 4532P Pulse Processor)
which limit the calibration variation to less than 0.01% for counting rates up to
10^4 x rays per second.

   The proton beam is collimated so that all protons which enter the target
chamber must pass through the target. The total charge which is accumulated in the
chamber during a measurement is recorded by a digital current integrator (Ortec
Model 439) and stored in the computer. The quantity of charge on each proton is
well known, so the computer converts the total charge into number of protons
passing through the sample. The computer also corrects for the number of events
lost due to pile-up (typically less than 3%).

Computer processing. The analysis process is monitored and the computer is controlled with an interactive video display. The first step in the analysis process is to subtract background radiation. Many experimental background spectrum are stored on a magnetic disk. The operator selects a background spectrum which represents the host material of the target being analyzed. The computer adjusts the background to match the target including the effect of the peak-tails described above. The background is then displayed on the video monitor as an overlay on the experimental data. Usually, the computer generated background accurately describes the actual background from the sample, but the operator can instruct the computer to refine the background by contacting the display with a "light pen".

The computer also has stored experimental data which describe the shape and the position of the characteristic x-ray peaks in the spectrum. Even though the imperfections in the detector response are small, they can be important for large peaks. The computer locates large peaks and identifies their tails and the false peaks that are produced by Si-escape x rays. Very large peaks can also produce false peaks due to simultaneous pile-up. The computer includes these refinements and performs a least square fit to the data to determine the number of x rays at each energy of interest. The stability of the energy calibration, the advanced knowledge of the shape of the characteristic x-ray peaks, and the careful treatment of imperfections and false peaks are all essential factors for accurate analytical results.

A typical spectrum for the lower energy portion of a coal ash sample is shown in Figure 1. The results of the computer fit is displayed on the video monitor as an overlay on the data. The operator can easily recognize any element which has been missed or incorrectly inserted and instruct the computer with the light pen to refine the fit to the data.

Most elements emit two or more x rays (for example, notice the two peaks from Sr identified in Figure 1). The relative heights of these peaks have all been measured experimentally for single element calibration targets. The computer checks that the fit to the sample data agrees with these standards. The computer also looks for possible sources of error due to two x rays which have approximately the same energy. All of this information is printed out for the operator to evaluate the reliability of the analysis.

After the operator has approved the analysis of a sample, the computer uses the number of protons passed through the target and stored calibration tables for the proton energy and filter conditions to determine the weight of each element in the sample. These weights are divided by the total sample weight to calculate the fractional weight of each element.

System calibration. The basic relation which must be known to obtain analytic results is the number of x rays detected, per unit of protons, per unit of weight of the element. This x-ray yield has been measured for a fixed detector position, for each proton energy, and each filter condition. Thin film calibrators (typically 100 μgrams/cm^2) are used so that it is not necessary to correct for slowing down of the protons or x-ray absorption in the calibrators. Thirty metal films of known weight deposited on Mylar were obtained from Micromater Inc. Thirty five calibrators were made in our laboratory from commercial atomic absorption liquid standards. The x-ray yield is a slowly varying function of atomic number. The results of yield measurements for each proton energy and filter condition were least square fit to an algebraic function to obtain yield curves for all elements from Al to Pu. The RMS deviation of the individual measurements around the best-fit function was typically 3%. Gamma-ray yields were measured for each light element that is detected by γ rays.

51

X-RAY SPECTRUM
COAL ASH
4 MeV PROTONS

COUNTS/CHANNEL

X-RAY ENERGY
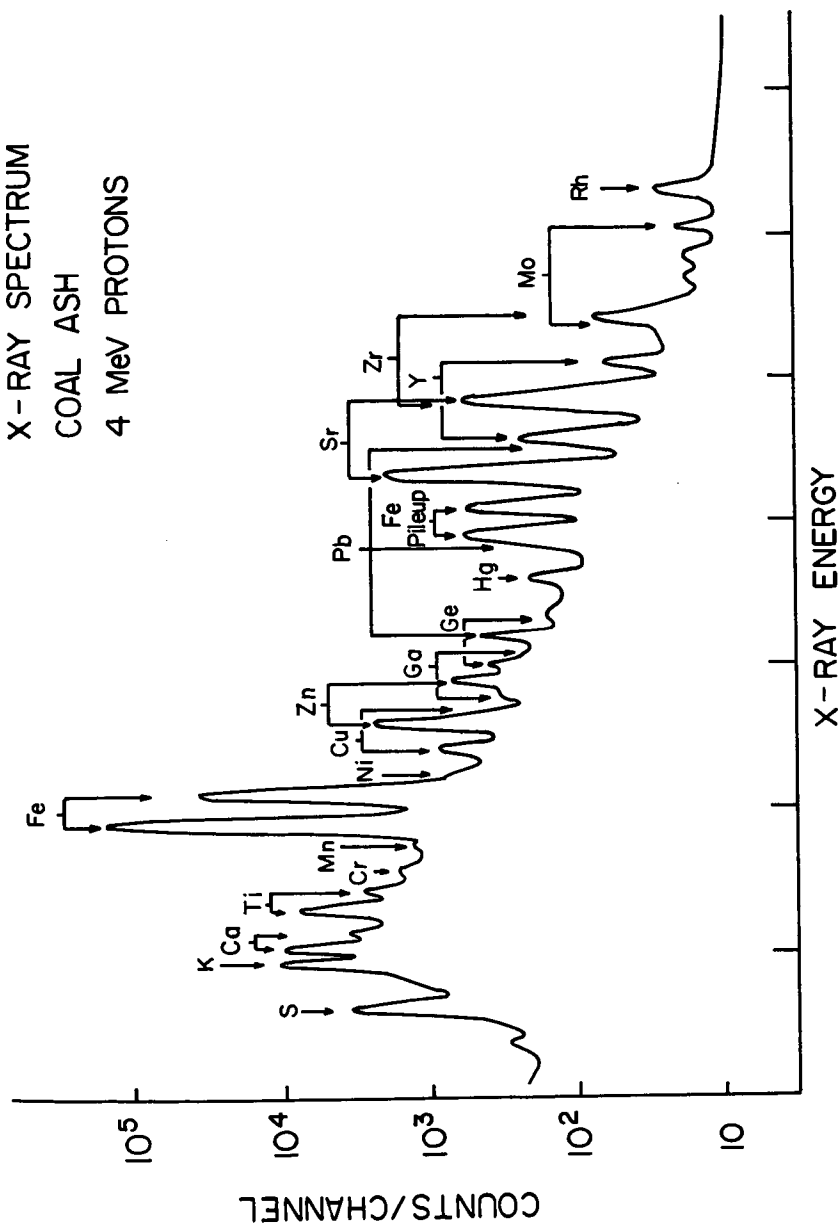
Limitations to analysis. As noted above the x-ray counting rate is limited by the noise filter which is essential for good energy resolution. Thus the number of x rays that can be observed from trace elements in a fixed time period will be limited by intense radiation from an abundant element. Analysis cost are directly effected by bombardment time, so the most practical solution is to reduce the intensity of the dominant radiation with an absorber. Energy selective filters can be useful for special problems, but the best general technique is to select a material where the probability of absorption decreases rapidly with increasing energy. The unwanted x ray can be controlled, but all lower energy x rays will be lost. However, higher energy x rays will be retained with minimum loss. Carbon is a good filter material and it is conveniently available in thin plastic films.

For coal samples we detect all elements heavier than Fe with 4 MeV protons and a 5 mm thick plastic filter to absorb Fe x rays. Elements from Al to Fe are observed in a separate measurement with 2.5 MeV protons. There is some x-ray absorption due to the windows which separate the target and detector. It would not be desirable to eliminate these windows because they prevent scattered protons from reaching the x-ray detector. The high intensity x rays from Fe and S in coal limit the data rate that can be obtained for light elements. However, light elements are frequently relatively abundant and their x-ray yields are large so good results can be obtained for most elements.

In some cases an intense x ray from and abundant element or a false peak due to simultaneous pile-up will have approximately the same energy as a low intensity x ray from a trace element. Then the sensitivity for that trace element will be limited to a fraction of the abundant element. These limitations are predictable so they can be included in the specifications for PIXE analysis.

Detection limits. The sensitivity is determined primarily by the time that the target is exposed to the proton beam. Other significant factors are background radiation, the presence of elements in high concentration, and energy interference for a few elements. The detection limit is relatively poor for P (approximately 250 ppm) but it rapidly improves to approximately 2 ppm for Cr, Mn, and Fe. The detection limit is approximately 1 ppm for most elements from Co to I, approximately 10 ppm for the rare-earth elements, and typically 3 ppm for the heavy metals up to Pu. The detection limit using γ rays for the light elements Li, B, F, Na, Mg, Al, and Si is usually a few ppm.

Results obtained for the analysis of NBS standard reference material 1632 (coal) are given in Table 1. The cost for this type of analysis would be $30 to $80 per sample depending on the number of samples that were analyzed.

In summary, PIXE is a powerful technique for multielemental analysis of a wide variety of samples. Very light elements can be observed by detecting γ rays and x rays in the same experiment. Although the original cost of the equipment is very large, there are many laboratories which already have the required facilities. After the system is developed the cost of analysis is low compared to other multielemental techniques of comparable sensitivity.

Table 1

Analysis of NBS Standard Reference Material 1632 (Coal) by PIXE

Results given in parts per million by weight

| Element | Purdue PIXE | | NBS Value | |
	N Result	ΔN Uncertainty	N	ΔN
Al	17600	1500		
Si	34000	4000	32000	
S	11300	1000		
Cl	850	80		
K	2540	250		
Ca	3500	300		
Ti	890	90	800	
V	35	3	35	3
Cr	17	3	20.2	.5
Mn	36	3	40	3
Fe	7900	800	8700	300
Co	10	6	6	
Ni	15.6	1.5	15	1
Cu	16	1.5	18	2
Zn	33	3	37	4
Ga	5.3	0.5		
Ge	2.4	0.3		
As	5.0	1	5.9	.6
Se	3.0	.3	2.9	.3
Br	20.5	1		
Rb	18.9	1		
Sr	140	10		
Y	7.5	.5		
Zr	35.5	1.5		
Nb	2.2	0.5		
Mo	2.2	0.5		
Ag		≤ .3		≤ 0.1
Cd	0.5	0.3	.19	.03
Sb	3.0	1		
Ba	310	30		
La	15	5		
Hg		< 1	.12	.02
Pb	23	4	30	9
Th	3.7	1	3.0	
U	2.1	1	1.4	.1

SIMULTANEOUS DETERMINATION OF MAJOR, MINOR AND TRACE CONSTITUENTS IN COAL ASH BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY. <u>V. A. Fassel</u>,

E. M. Layton, and E. L. DeKalb, Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The present status of the simultaneous determination of major, minor, and trace elemental constituents in coal ash by the inductively coupled plasma-atomic emission spectroscopy technique will be reviewed. The coal ash samples are brought into solution either by lithium metaborate fusion or by a perchloric-nitric-hydrofluoric acid dissolution procedure. The relative merits of these two procedures will be discussed. Linear analytical calibration curves covering concentration ranges of three or more decades are obtained. Corrections for stray light effects may be required unless these background contributions are reduced to negligible proportions through the selection of appropriate gratings and for the use of interference filters. Analytical data in reference coal samples will be discussed.

Comparison of Atomic Absorption and D.C. Plasma-Arc Spectrometry in Multi-Element Analysis of Coal

Norman H. Suhr and Henry Gong

Mineral Constitution Laboratories, 310 Mineral Sciences, The Pennsylvania State University, University Park, PA 16802

As part of a project at The Pennsylvania State University to characterize the inorganic constituents of American coals, an analytical scheme was developed whereby most of the major and minor elements (Si, Al, Fe, Ca, Mg, Ti, Mn, Na, K) in high temperature (750°C) coal ashes were determined by atomic absorption spectrophotometry (A.A.S.) and most of the trace elements (Ba, Be, Co, Cr, Ga, Ge, La, Mo, Ni, Pb, Sc, Sn, Sr, V, Y, Yb and Zr) determined by d.c. arc emission spectrography. However, after the acquisition of a d.c. argon plasma spectrometer, a study was conducted to determine whether this instrument was capable of assuming some of the functions of the atomic absorption unit or emission spectrograph. This was done because emission spectrometry offers many advantages over A.A.S. and conventional emission spectroscopy, primarily in the area of rapid analysis of sample. Whereas in A.A.S., only one element can be determined at a time, emission spectrometry has the capability of performing simultaneous multi-element determinations (up to 18 at one time for the instrument in this study). In addition, the emission spectrometer, unlike the emission spectrograph, has a direct numerical readout which is much more amenable to efficient data handling and manipulation than the conventional photographic plates. This, in turn, coupled with a more stable excitation source, leads to greater precision among different sets of data. Additionally, the superior dispersion (between 0.61 and 2.44 A/mm in the 2000-8000 a range) of the echelle grating eliminates many of the spectral interferences common to other spectrographs. Emission spectrometry is also, unlike A.A.S., not limited by hollow cathode lamps, does not employ explosive gases, and because of the higher source temperature, has fewer chemical interferences.

Because the plasma emission spectrometer accepts only liquid samples, it was decided to initially compare the instrument with A.A.S. The emission spectrometer employed here is the Spectrametrics Incorporated (SMI) Spectraspan III in which the excitation source consists of a high temperature (up to 10,000 K, typically 6000°K in the analytical region) d.c. argon plasma. The instrument nebulizes liquid samples with argon and introduces the aerosol into the plasma at a constant rate by means of a peristaltic pump. The emitted radiation is dispersed in the spectrometer by an echelle grating, the orders separated by a quartz prism and channeled into a series of photomultiplier tubes each of which are set so as to receive the radiation at one particular wavelength characteristic of each of the various elements of interest (e.g. Cu is determined by monitoring the Cu 3274 line in the 69th order, Mn by monitoring the Mn 2576 line in the 88th order, etc.)[*] The capability also exists for adjusting the system so that elements other than the 18 pre-set elements can be determined. The photomultiplier tube outputs for the various elements are connected with a micro-computer which manipulates the received data according to various programs (e.g. integration over a period of time, use of an internal standard, etc.) and prints out the results on an auxiliary printer. The raw data (arbitrary units in the range 0-9999) may also be printed out if so desired.

The sample preparation for the plasma spectrometer is essentially the same as that used for A.A.S. (1). The high temperature ash (750°C) of the test coal was ground to -200 mesh (<74 μ) to ensure sample homogeneity and a 200 mg sample was mixed with 800 mg of $LiBO_2$ and fused at 1050°C for 10 minutes; the resultant molten bead is then poured directly into 80 ml of a 4% HNO_3 solution. For plasma spectrometry, 6 replica solutions were prepared from this initial solution by taking six 5.00 ml aliquots and diluting each with 35.0 ml of a solution consisting of 0.5% Li

---

[*] Analytical lines are listed in Table 1.

56

Table 1. Analytical Lines Used for the Emission Spectro-
metric Analysis of Coal Ashes

Element	Wavelength (A)	Order
Al	3961	57
Ba	4554	50
Ca	3179	71
Cu	3247	69
Fe	2382	95
Ge*	2651	85
K	7698	29
Mg	2795	80
Mn	2576	88
Na	5895	38
Si	2516	90
Sr	4077	55
Ti	3349	67
Zn	2138	106
Zr	3601	62

*Used as internal standard.

in 2% nitric acid and containing 10 ppm Ge. The Li content of the final solution is
about 4500 ppm and serves as an effective spectroscopic buffer while the Ge acts as
an internal standard. Six replica solutions were also prepared for A.A.S. by dilut-
ing 5.00 ml aliquots of the initial solution with 30.0 ml of a 10,800 ppm La solu-
tion, the La acting as a releasing agent in the flame process. The appropriate sets
of solutions were then ready to run on the plasma spectrometer and A.A. spectrophoto-
meter along with sets of standards prepared in the same manner as the samples. How-
ever, the nature of the electronics on the plasma spectrometer is such that prior to
the running of the solutions, it was necessary to calibrate the instrument with
standards containing approximately the highest concentrations of the elements that
one would expect in the solutions. Once so calibrated the instrument automatically
extrapolates linearly between the calibrated maximum point and a blank to give a
reading for each solution run. If, however, this calibrated upper limit should be
exceeded by more than about 25% by a solution, no reading will be produced and the
solution must be diluted before it can be analyzed. Although, in theory, only one
standard need be run for the emission spectrometer, at least three or four were run
as a check against both possible line curvature (e.g. distortion due to self-absorp-
tion) and errors in the preparation of any one standard. All of the standards used
are shown in Table 2.

During the actual running of solutions in both plasma emission spectrometry and
A.A.S., the standards were run first, then the six samples, then the entire set of
solutions in reverse order so that two runs were performed on each solution. This
was done to cancel out any instrumental drift which might occur from the first to
the last sample. The results of three sets of runs; one set on the plasma spectro-
meter with the internal standard function off, one set with the internal standard on,
and one set on the atomic absorption unit, are presented in Table 3.

Each number in Table 3 represents the mean of 6 replicas and is given ± 2 stand-
ard deviations. While the plasma spectrometer is theoretically capable of simul-
taneously determining all of the elements listed, in practice it was found that
usually no more than 5 or 6 elements could be comfortably handled at any one time
due to variations in the instrumental calibrations for each element over a long
period of time (one-half hour or so). Consequently, the elements Fe, Mg, Ca, and
Mn were run as a group while Si, Al, K and Na formed a second group. By A.A.S.
of course, each element was determined separately. The results show that with the
exception of Fe, all of the elements determined overlap each other within the 2σ
significance range. Although no explanation can be given for the difference in iron
values by A.A.S. and emission spectrometry, a titrimetric determination on another
sample split gave a value of 4.37% Fe_2O_3 which is more in agreement with the emission
spectrometric results. Table 3 also shows that the magnitude of the standard devi-
ation tends to be significantly greater for the atomic absorption determinations
than it is for either of the sets of data obtained from plasma emission spectrometry.

This is especially true for silica. Although part of the scatter may be explained by the observation that the silicon hollow cathode lamp was beginning to fail, the standard deviations obtained for silica in rocks and coal ashes by plasma emission spectrometry are nevertheless better than those obtained by A.A.S., even under optimum conditions. No attempt was made to rigidly define and compare detection limits for the various elements by emission spectrometry and atomic absorption because such limits tend to be affected by many factors which are easily altered (e.g. sample composition, gas flow and pressure, optical alignment, electronic stability, etc.). However, on the basis of observations made during this study, and ignoring the major constituents, it can generally be said that those elements that have strong emission lines or form refractory oxides are determined better at low concentrations by plasma emission spectrometry than by A.A.S.

The results in Table 3 also indicate that the standard deviations for the plasma spectrometric determinations in which an internal standard was employed tend to be somewhat better than those in which no internal standard was used, although the differences do not appear to be statistically significant.

Some studies here as to whether or not the plasma spectrometer is capable of adequately determining some trace elements currently done by conventional d.c. arc spectrography indicate that the elements Ba, Cr, Cu, Sr, V and Zr may be done on the spectrometer. In addition to the previously mentioned advantages of using the spectrometer, the initial results indicate that an improvement in precision also results. This is probably because of two factors, the first of which is the use of a more stable excitation source and second, the use of a larger sample size. A 200 mg sample is taken for the fusion technique while only 6 mg of sample is used per electrode for spectrographic analysis. The use of a greater sample size assumes added significance where trace elements tend to be concentrated in inhomogeneously distributed accessory minerals (e.g. Zr in zircon) (2).

Despite the use of a greater initial sample size, however, the dilution of the sample during sample preparation is considerably greater for the spectrometer than it is for the spectrograph. Consequently, the absolute quantities of the sample excited in the spectrometer are much less than that in the spectrograph. Because of this, the conventional spectrograph is still to be preferred for trace elements which are present in minute quantities such that when diluted, would fall below the detection limits of the spectrometer. However, since detection limits, as stated above, tend to be variable in nature, it is not possible to specify the concentrations of each element below which the spectrograph is to be preferred. This must be left to the judgement of the individual operator and laboratory.

Acknowledgment

Literature Cited

1. Medlin, J. H., Suhr, N. H., and Bodkin, J. B., At. Absorpt. Newslett. (1969), $\underline{8}$, 25.
2. Ondrick, C. W. and Suhr, N. H., Chem. Geol. (1969), $\underline{4}$, 429.
3. "Analytical Methods for A.A.S.", (1973), Perkin-Elmer Company, Norwalk, Conn.

Table 2. Standards Used in Plasma Spectrometric and Atomic Absorption Analyses of High Temperature (750°C) Coal Ashes

STD	SiO2	Al2O3	Fe2O3	CaO	MgO	MnO	K2O	Na2O	TiO2	Cu	Ba	Sr	V	Zn	Zr
G-2	69.2*%	15.1%	2.75%	2.00%	0.76%	0.034%	4.50%*	4.05%*	0.50%	-	1860ppm	477ppm	34ppm	-	300ppm
PCC-1	-	-	-	-	-	-	-	-	-	-	169	198	-	36ppm	-
W-1	52.6	15.0	11.06	10.96	6.52	0.175	0.63	2.15	1.08	110ppm	579	-	260	86	105
T-1	62.6	16.2	5.88	5.12	1.82	0.100	1.23	4.32	0.56	-	1080	1350	-	160*	170
BR	38.3	10.25	12.9*	13.9*	13.34*	0.205*	-	-	2.62*	72	-	-	240	160	-
NBS98	59.1	25.54	2.05	0.21	0.72	0.005	3.17	0.26	1.43	-	-	-	-	-	-
BR:NBS98 1:1	48.7	17.9	7.48	7.06	7.04	0.105	2.29	1.67	2.03	-	-	-	-	-	-
NBS98A	48.9	33.2*	-	-	-	-	1.04	0.082	-	-	-	-	-	-	-
NBS97	-	-	-	-	-	-	-	-	-	-	-	-	224	-	-
PSOC364	-	-	-	-	-	-	-	-	-	317*	2320*	5000*	400*	-	1850*
PSOC364:Blank 1:1	-	-	-	-	-	-	-	-	-	158	1160	2500	200	-	-
Blank+	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Used for high standard calibration of plasma spectrometer

+Blank is spec-pure silica

G-2 (granite), PCC-1 (peridotite), W-1 (basalt) are U.S. Geological Survey rock standards, T-1 is a tonalite rock std from Tanganyika, BR a basalt from the Centre de Recherches Petrographiques at Geochemiques, France, NBS97 and 98 are clays from the U.S. National Bureau of Standards and PSOC364 in a coal ash.

Table 3. Comparison of Atomic Absorption* and Plasma Spectrometric* Data from a Coal Ash (PSOC 361)

	d.c. Plasma Spectrometry		Atomic Absorption Spectrophotometry
	No Internal Standard	Internal Standard (Ge)	
SiO2	61.0% ± .8	60.6% ± .5	57.5% ± 5.6
Al2O3	27.6 ± .7	26.7 ± .5	27.1 ± .4
Fe2O3	4.28 ± .04	4.37 ± .04	4.54 ± .06
CaO	0.794 ± .008	0.798 ± .016	0.844 ± .046
MgO	0.861 ± .014	0.868 ± .010	0.875 ± .014
MnO	0.018 ± .0004	0.018 ± .0004	0.018 ± .002
K2O	2.69 ± .036	2.65 ± .030	2.58 ± .042
Na2O	0.767 ± .050	0.753 ± .048	0.813 ± .064

Each value given represents the mean of six sub-samples ± 2 standard deviations.

* Atomic Absorption unit employed was a Perkin-Elmer Model 403, instrumental parameters for A.A.S. were as stated in the Perkin-Elmer manual (3) with the exception of Ca for which a N_2O-C_2H_2 flame was used instead of the recommended air-C_2H_2. The plasma spectrometer was a Spectrametrics Spectraspan III.

TRACE METAL ANALYSIS IN COAL BY MULTIELEMENT ISOTOPE
DILUTION SPARK SOURCE MASS SPECTROMETRY

J. A. Carter, D. L. Donohue and J. C. Franklin

Oak Ridge National Laboratory*
Post Office Box Y
Oak Ridge, Tennessee   37830

INTRODUCTION

The use of spark source mass spectrometry for the analysis of environ-
mentally important elements found in coal and fly ash is described. Significant
improvement in the accuracy and precision of the method has been accomplished by
use of isotope dilution methods for several elements in a sample. As many as 20
elements have been simultaneously determined in certain energy-related samples
using multielement isotope dilution SSMS. The precision and accuracy are typi-
cally ±5-10% RSD for elements present at greater than 1 part per million in the
sample.

For those samples which are difficult to dissolve cleanly, it is not pos-
sible to apply the classical isotope dilution technique. Rather, the dry material
is mixed with a 'spiked' conducting matrix containing separated isotopes of the
elements of interest.   This method combines ease of sample handling with certain
desirable aspects of separated isotopes—namely their freedom from contamination
effects. Here the precision obtained is typically 10-15% RSD and the accuracy de-
pends on the use of appropriate standards.

EXPERIMENTAL

For an isotope dilution analysis, the following steps are taken:

1. Complete dissolution of the sample in a high purity acid (HNO_3, HCl).
2. Addition of accurately standardized separated isotope 'spikes.'
3. Isotopic equilibration by chemical or thermal means.
4. Mass spectrometric analysis.

The important step is number three, because it is assumed that once equilibration
has occurred, the separation or concentration steps that follow need not be quanti-
tatively known. It is also assumed that the equilibrated spike and sample isotopes
will behave in an identical fashion, both chemically and in the ion source of the
mass spectrometer.

Coal and fly ash analysis by this method depends upon sample dissolution.
Unfortunately, the acids required to completely dissolve these materials (HF, $HClO_4$,
H_2SO_4) are difficult to obtain in a pure form and also produce undesirable molecular
ion species in the spark source. High pressure dissolution in a teflon lined pres-
sure bomb (Parr Instrument Co.) using HNO_3 and HCl has been tried, but silicate
species are usually not soluble under these conditions. Other methods, such as
NaOH fusion followed by HCl treatment produced clear solutions, but these contained
an unacceptable amount of NaCl which gave rise to mass spectral interferences.

Because of the difficulty of dissolving these materials, a dry mixture technique was developed,[1-3] which involves the use of a 'spiked' matrix material such as high purity Ag or graphite. Separated isotopes of the elements of interest were dried from solution onto the matrix and vigorous shaking in a ball mill ensured homogeneity.   This spiked matrix was analyzed alone in order to determine the blank levels and was then mixed with standards (NBS SRM 1632 Coal or 1633 Fly Ash) to determine the amount of each isotope added. This standardization also provided any relative sensitivity corrections which were necessary in this technique.

Table I shows the composition of a spiked Ag matrix (99.9999% pure Ag Cominco American, Inc.) which was used in the analysis of coal (after ashing at 500°C in air to remove the organics) as well as fly ash.   The isotopes chosen were usually minor ones in nature which were highly enriched and chosen to be free of spectral interference.

The instrumental operating parameters are summarized below:

Instrument: AEI MS-702R with photographic plate detection.
Spark conditions: 30 kV rf; 100 pulses per second, 25 μsec pulse length.
Vacuum: Source $<1 \times 10^{-4}$ torr; analyzer 2×10^{-8} torr.
Photoplate: Ilford Q2 or Kodak SWR.
Development: 3 minutes in conc. D-19.

A photoplate data reduction system was used which utilized a minicomputer interfaced with a microdensitometer.[4]   The computer accepts digitized optical transmittance data as the densitometer scans over a line. It then computes peak height corrected for background and converts this into relative (ion) intensity using a stored calibration curve (Churchill two-line calibration method[5]).   The relative (ion) intensities are employed in the computer code to obtain elemental concentrations according to the Hintenberger[6] isotope dilution equation.

The concentration of the element being measured is obtained from the following equation.

$$x = y \left(\frac{R_t - R_m}{R_m - R_s}\right) \cdot \frac{A_s}{A_t} \cdot \frac{T}{S} \qquad\qquad 1)$$

where x = weight of element in the sample.

y = weight of element in the tracer spike.

R_t = isotope ratio of the spike, $\dfrac{\text{reference isotope}}{\text{tracer isotope}}$.

R_m = isotope ratio of the mixture, $\dfrac{\text{reference isotope}}{\text{tracer isotope}}$.

R_s = isotope ratio of the sample, $\dfrac{\text{reference isotope}}{\text{tracer isotope}}$.

A_s = atomic weight of the sample element.

A_t = atomic weight of the tracer.

T = atom % of the spike isotope in the tracer.

S = atom % of the spike isotope in the sample.

The terms: A_s, A_t, T, S, R_s, R_t, and y are usually known in advance, and since R_m can be very accurately measured, it is not unusual to obtain precision and accuracy on the order of 5% for trace element determinations. After equilibrium between spike isotope and sample reference isotope is obtained, quantitative results are assured by isotope dilution even when a low yielding chemical purification is required.

RESULTS AND DISCUSSIONS

Table II shows results for NBS SRM 1632 using the dry spike technique, with SRM 1633 acting as the standard. The results agree within experimental precision for all elements shown. It was possible to analyze a number of other elements by the same technique, provided the concentration in the standard was known with some certainty. In all, twelve elements are routinely reported in coal by this method with a precision and accuracy of about ±15% RSD.

Any analysis of coal or fly ash by SSMS is subject to mass spectral interference arising from the major elements present. These include Si, Al, Ti, Mg, Fe, Na, K and S. Combinations of these elements, oxides, silicates and chlorides, as well as molecular ions from the matrix element (Ag_2^+, AgO^+) must all be considered for their potential effect on the analysis. Certain elements are generally always interfered with (Co^+ by CaF^+ and Sb^+ by AgO^+), while other isotopes are only occasionally affected. Therefore, if a small number of elements is to be analyzed, the analyst should consider using separation and concentration methods to eliminate possible interferents.

REFERENCES

1. Jaworski, J. R., and Morrison, G. H., Anal. Chem. 47 (1975) 1173.
2. Donohue, D. L., Carter, J. A., and Franklin, J. C., Anal. Letters (1977), in press.
3. Carter, J. A., Donohue, D. L., Franklin, J. C., and Walker, R. L., in Analytical Methods for Coal and Coal Products, Academic Press, N. Y. (1977).
4. Carter, J. A., Franklin, J. C., and Donohue, D. L., ACS Symposium Series (1977), in press.
5. Churchill, J. R., Ind. Eng. Chem., Anal. Ed., 16 (1944) 653.
6. Hintenberger, H., in Electromagnetically Enriched Isotopes and Mass Spectrometry, (M. L. Smith, ed.), Academic Press, Chap. 21 (1956) 177-189.

Table I

Spiked Silver for Coal and Fly Ash Analysis

Element	Isotope	Enrichment	Nominal Concentration
Pb	204	99.7	10 ppm
Tl	203	94.9	5
Ba	135	93.6	50
Te	125	91.2	10
In	113	96.4	5
Cd	111	91.3	5
Mo	97	94.3	5
Sr	86	95.7	100
Se	77	94.4	10
Zn	67	89.7	30
Cu	65	99.7	30
Ni	61	99.5	30
Fe	57	93.6	100
Cr	53	96.4	30
K	41	99.4	200

Table II

Analysis of SRM 1632 Using SRM 1633 as Standard

Element	Conc. in µg/g ± RSD	NBS Certified
Tl	0.6 ± 0.2	0.59 ± 0.03
Pb	33 ± 3	30 ± 9
Cd	0.4 ± 0.2	0.19 ± 0.03
Zn	32 ± 8	37 ± 4
Cu	15 ± 3	18 ± 2
Ni	15 ± 3	15 ± 1
Cr	19 ± 3	20.2 ± 0.5

Recent Application of Neutron Activation Analysis to Coal

Hugh T. Millard, Jr.

U.S. Geological Survey, MS 424, Box 25046
Denver Federal Center, Denver, Colorado 80225

The possibility of environmental contamination resulting from current and proposed uses of large quantities of coal for combustion, liquefaction, and gasification has been discussed extensively. In order to evaluate the potential for harm, many studies have been undertaken to determine the trace-element compositions of various coals and the elemental budgets of coal-consuming facilities, such as power plants. Neutron-activation analysis has been used extensively for these studies, because the method has good sensitivity for a large number of elements of interest, is nondestructive, and, when automated, can be used to process samples rapidly and efficiently.

In common with other analysts, the activation analyst strives to reduce interferences and determine the elements of interest. The methods used to discriminate among the large numbers of radioactive nuclides produced by neutron bombardment are listed in Table 1. Such an outline is useful for a general discussion of neutron-activation analysis, but variations of the techniques may deviate from this table. Because of the large numbers of coal samples that must be analyzed, instrumental techniques have been employed whenever possible to avoid time-consuming radiochemical separations and the possibility of loss of volatile elements.

Although all of the techniques in Table 1 are instrumental, with the exception of radiochemical neutron-activation analysis (RNAA), the term instrumental neutron-activation analysis (INAA) is ordinarily reserved for the method in which gamma-spectra are collected using high-resolution gamma-detectors (lithium-drifted germanium or intrinsic germanium) at different decay times following neutron bombardment of the sample. This technique allows the determination of as many as 40 elements in coal and fly ash, and many such multi-element procedures have been reported (1-10). The elements determined include Al, As, Au, Ba, Cr, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, and Zn. However, about seven of these elements (Au, Ba, Ga, Ni, Rb, Ti, and Zn) exist in some coal at concentrations near their limits of detection, and, therefore, the exact number of elements that can be determined depends on the composition of the individual coal sample. The U.S. Geological Survey used INAA to determine many of the elements listed above in eighteen coal samples from various locations in the United States (11) and, more recently, as one of the analytical techniques for routine analysis of 2,000 Eastern U.S. coal samples. However, special emphasis is placed on determining As, Cr, Co, Sb, and Se, because these elements are more difficult to determine by other analytical techniques.

If a sample is surrounded with Cd during neutron bombardment, then activation by epithermal neutrons is enhanced relative to that by thermal neutrons and some selectivity may be achieved. This technique has been used to determine U and Th in coal and coal ash (12, 13). At the U.S. Geological Survey, Rowe and Steinnes made an extensive study of the activation analysis of coal and fly ash that included a comprehensive comparison of thermal and epithermal INAA (10). They found that the sensitivities for Ba, Cs, Ga, Hf, Ho, In, Mo, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, and Zr were improved when epithermal INAA was employed.

Fast neutrons (14 MeV) from a neutron generator may be used to activate light elements. O, N, F, Si, and Al have been determined in coal by this rapid and routine technique (14-17). Because the distribution of O between the organic and mineral components of coal is highly variable and because the other elements are determined by other routine techniques, the fast neutron method is seldom used in coal analysis.

Prompt gamma-counting (PG) involves detecting the gammas emitted immediately after neutrons are absorbed during bombardment. This method has been used to determine Fe, B, and Cd in coal (18, 19).

The delayed-neutron counting technique (DN) is used (20) primarily to determine U and Th. One-minute neutron irradiations are followed by several minutes of counting the neutrons emitted by the fission-daughters of U and Th. Thermal and epithermal neutron irradiations are performed to differentiate between U and Th. At the U.S. Geological Survey, we use automated neutron counters to analyze about 7,000 samples per year by this technique (11, 21). Using 5-g coal samples, the carbon matrix causes neutron thermalization within the sample, so it is important to prepare standards by spiking a suitable coal with U and Th. We maintain good accuracy by intercalibration with isotope dilution-mass spectrometric U and Th standards.

Uranium may also be determined by fission-track (FT) counting (22). This technique is very useful for small samples (<100 mg), such as mineral separates. We have automated this procedure by using spark-counting or more recently, by employing an image analyzer. Fission-track maps of pellets prepared from coal powders indicate whether the U is distributed evenly in the organic matrix or is concentrated in discrete mineral phases such as apatite. Maps of thin sections of coal can be used to find minerals containing high concentrations of U, and these minerals may then be identified by suitable techniques such as electron-microprobe analysis.

Radiochemical neutron-activation analysis (RNAA), in which radiochemical separations are performed after neutron irradiation and prior to counting, has been used to determine As, Br, Cd, Cs, Hg, Ga, Rb, Sb, Se, U, and Zn in coal (23, 24). However, in recent years these methods have been replaced to a great extent by the faster and less tedious instrumental techniques discussed above. RNAA still is used for several elements (e.g., Hg and Cu) for which instrumental methods are not sufficiently sensitive (6, 25), and to calibrate standard materials when the highest levels of precision and accuracy are required.

Table 1. Methods of discrimination employed in various neutron-activation analysis techniques

INAA = Instrumental Neutron Activation Analysis
FNAA = Fast Neutron-Activation Analysis
PG   = Prompt Gamma-Counting
DN   = Delayed Neutron Counting
FT   = Fission Track
RNAA = Radiochemical Neutron-Activation Analysis

Method of Discrimination	INAA Thermal	INAA Epithermal	FNAA	PG	DN	FT	RNAA
Energy of bombarding neutrons:							
thermal (0.1 eV)	X			X	X	X	X
epithermal and resonance (0.1-1000 eV)		X			X		X
fast (14 MeV)			X				
Irradiation time	X	X	X		X		X
Decay time after irradiation	X	X	X		X		X
Emitted particle measured:							
gamma (spectrometry)	X	X	X	X			X
neutron					X		
fission fragment						X	
Chemical properties							X

References

1. Block, C., Dams, R., "Determination of Trace Elements in Coals by Instrumental Neutron Activation Analysis", Anal. Chim. Acta (1973) 68, 11-24.

2. Weaver, J. N., "Determination of Mercury and Selenium in Coal by Neutron Activation Analysis", Anal. Chem. (1973) 45, 1950-2.

3. Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talmi, Y., VanHook, R. I., Bolton, N., "Pathways of Thirty-seven Trace Elements Through Coal-Fired Power Plant", Environ. Sci. and Technol. (1975) 9, 973-9.

4. Abel, K. H., Rancittelli, L. A., "Major, Minor, and Trace Element Composition of Coal and Fly Ash, as Determined by Instrumental Neutron Activation Analysis", Advances in Chemistry Series 141, Trace Element Fuel Symposium 1973 (1975), 118-138.

5. Sheibley, D. W., "Trace Elements by Instrumental Neutron Activation Analysis for Pollution Monitoring", Advances in Chemistry Series 141, Trace Elements Fuel Symposium 1973 (1975), 98-117.

6. Ruch, R. R., Cahill, R. A., Frost, J. K., Camp, L. R., Gluskoter, H. J., "Survey of Trace Elements in Coals and Coal-Related Materials by Neutron Activation Analysis": paper presented at the 1976 International Conference: Modern Trends in Activation Analysis, Munich, Sept. 1976.

7. Kucera, E. T., Heinrich, R. R., "Multielement Trace Analysis of Coals, Ashes, and Related Materials from Coal-Treatment Facilities by Instrumental Neutron Activation Analysis", J. Radioanal. Chem. (1976) 32, 137-150.

8. Filby, R. H., Shah, K. R., Sautter, C. A., "A Study of Trace Element Distribution in a Coal Conversion Process Using Neutron Activation Analysis": Paper presented at the 1976 International Conference: Modern Trends in Activation Analysis, Munich, Sept. 1976.

9. Obrusnik, I., Starkova, B., Blazek, J., "Instrumental Neutron Activation Analysis of Fly Ashes and Emissions", J. Radioanal. Chem. (1976) 31, 495-502.

10. Rowe, J. J., Steinnes, E., "Instrumental Activation Analysis of Coal and Fly Ash with Thermal and Epithermal Neutrons": Paper presented at the 1976 International Conference: Modern Trends in Activation Analysis, Munich, Sept. 1976.

11. Millard, H. T., Jr., Swanson, V. E., "Neutron Activation Analysis of Coals using Instrumental Techniques", Abstract in Transactions of the American Nuclear Society, v. 21, 1975 Annual Meeting, New Orleans, 108-109.

12. Ganzorig, Zh, Dashzeveg, L., Otgonsuren, O., Khuukhenkhuu, G., Chadraabal, I., Chultem, D., "Nondestructive Determination of a Trace Amount of Uranium and Thorium in Materials of Complex Chemical Composition", Radiokhimiya (1974) 16, 247-53.

13. Erdtmann, G., "Determination of Uranium and Thorium in Coal Ash and Power Station Precipitator Ash and in Bauxite and Red Sludge by Activation Analysis with Epithermal Neutrons", Kerntechnik (1976) 18, 36-40.

14. Botvina, A. Ya., Sokol'skii, V. V., Faizrakhmanova, N. R., "Determination of Nitrogen and Fluorine by Using Fast Neutrons", Aktiv. Anal. Mater. Vses. Soveshch., 2nd 1968 (1971), 189-91.

15. Loska, L., Gorski, L., "Determination of Ash Content of Coal by Neutron Activation Analyses", Radiochem. Radioanal. Lett. (1972) 10, 315-22.

16. Kut, D., "Determination of Oxygen in Coal by Fast Neutron Activation Analysis", Tech. J.-Ankara Nucl. Res. Cent. (1975) 2, 96-104.

17. James, W. D., Ehmann, W. D., Hamrin, C. E., Chyi, L. L., "Oxygen and Nitrogen in Coal by Instrumental Neutron Activation Analysis", J. Radioanal. Chem. (1976) 32, 195-205.

18. Pak, Yu. N., Starchik, L. P., "Neutron-radiation Determination of the Iron Content in Coals", Koks Khim. (1974) 10-11.

19. Gladney, E. D., Jurney, E. T., Curtis, D. B., "Nondestructive Determination of Boron and Cadmium in Environmental Materials by Thermal Neutron - Prompt Gamma-Ray Spectrometry", Anal. Chem. (1976) 48, 2139-42.

20. Amiel, S., "Analytical Application of Delayed Neutron Emission in Fissionable Elements", Anal. Chem. (1962) 34, 1683-92.

21. Millard, H. T., Jr., "Determination of Uranium and Thorium in USGS Standard Rocks by the Delayed Neutron Technique", in U.S. Geol. Survey Prof. Paper 840 (1976) 61-65.

22. Fleischer, R. L., Price, P. B., Walker, R. M., "Nuclear Tracks in Solids", 605 pp., University of California Press, Berkeley, 1975.

23. Orvini, E., Gills, T. E., LaFleur, P. D., "Method for Determination of Selenium, Arsenic, Zinc, Cadmium, and Mercury in Environmental Matrices by Neutron Activation Analysis", Anal. Chem. (1974) 46, 1294-7.

24. Frost, J. Kennedy, Santoliguido, P. M., Camp, L. R., Ruch, R. R., "Trace Elements in Coal by Neutron Activation Analyses with Radiochemical Separations", Advances in Chemistry Series 141, Trace Element Fuel Symposium 1974 (1975), 84-97.

25. Dreesen, D. R., Wagnen, L. E. Gladney, E. S., Owens, J. W., "Solubility of Trace Elements in Coal Fly Ash": Paper presented at Environmental Chemistry and Cycling Processes, the Second Mineral Cycling Symposium, Augusta, Georgia, April 28- May 1, 1976.

A SURVEY OF EMISSION X-RAY ANALYSIS OF COAL

J. K. Kuhn and L. R. Henderson

Illinois State Geological Survey
Urbana, IL 61801

Measurement of emitted X-rays is finding widespread acceptance as an analytical tool for determining minor and trace elements in coal and coal-related materials. Because the method requires a short time for analysis and can determine concentrations ranging from a few parts per million up to 100% in a single sample, it is a desirable alternative to many other techniques (1).

Following the development of the method of Rose et al. (2), accurate analyses of coal ash have been routinely performed for several years. Methods for X-ray analysis of whole coal, however, despite earlier work by Sweatman et al. (3), have developed more slowly (4,5,6,7). Recent improvements in equipment, especially innovations in detectors and excitation sources, have brought about renewed interest in the technique.

Two types of spectroscopic systems are now available. One is the wave-length dispersive unit which uses crystals with various lattice spacings to diffract and separate the X-rays emitted from excited samples. A goniometer is then used in conjunction with either a gas-flow or a scintillation detector to measure the angle and intensity of the emitted radiation. The second type of system consists of a solid state detector, either lithium-drifted silicon or intrinsic germanium, connected to a multichannel analyzer. A typical detector, with resolution of 140ev to 160ev, produces pulses whose amplitudes can be separated and quantified for most X-rays. These systems, therefore, are capable of simultaneous multi-elemental analyses over a wide range of energies.

The X-ray tube, both with and without filters, is a common excitation source, but a number of other kinds of sources are useful. In systems where portability is desirable, isotope sources are commonly used with solid state detectors. These sources give nearly mono-chromatic exciting radiation which means that background corrections are smaller for effects due to scattered radiation and background. Decay of isotopes limits their useful life, but sources such as americium 241 (used with secondary targets) can provide resonably stable excitation for many years. Excitation by electron probe, ion probe, scanning electron microscopy, etc., is now widely used for X-ray analysis. Energetic protons, also used to induce X-ray emission, have the additional advantage of producing gamma radiation, which increases the number of elements that can be determined (8).

Regardless of the type of spectrometer or the exciting source used, a number of other problems must be solved before accurate analysis of coal and its related products can be obtained. Foremost among these is the problem of adequate standards. At present only two certified standards are available, one for trace elements in coal and one for trace elements in fly ash. This means that each laboratory must produce its own set of standards. Mathematical correction procedures may be applied instead but they are unsatisfactory when there are large variations in matrix. The second major problem is the acquisition of representative samples for analysis. Coal itself, is perhaps the simplest material to sample but still presents problems due to inhomogeneity. Variations within the coal seam or feed stock may limit precision to 5% (9), and the presence of discrete mineral particles may result in even greater errors (10). Coal-related materials - e.g. chars, ashes, residues, and products from liquefaction and gasification processes - vary greatly depending upon temperature,

physical location in the system, processing time, and other factors. These materials may range from nearly totally inorganic minerals to wholly organic liquids; occasionally a very viscous slurry that is almost impossible to homogenize is encountered.

The great variability of these materials causes not only sampling difficulties but also significant analytical problems. X-ray analysis is highly dependent upon matrix variations, which are normally handled in one of three ways. One solution is to prepare a sufficient number of standards so that every conceivable matrix can be very closely matched. Though this is not impossible, it is usually impractical for most laboratories.

A second method of handling the matrix problem is to prepare analytical samples in such a way as to make the variations almost insignificant. This may be done by dilution with an inert material (11), by addition of a heavy adsorber (2), or by preparation of a sample thin enough that all X-rays generated in the material will escape (6,8). The first two technqiues tend to raise the limit of detection of the trace elements in the original sample. Even though the third technique requires great care to prepare a uniform, representative sample, it is being used quite successfully by a number of laboratories.

The third method of correcting for matrix effects employs mathematical procedures. These procedures may be divided into three groups. The first includes various methods for empirically measuring the mass absorption coefficient of the material for the radiations of interest. These methods have been reviewed extensively by Lubecke (12) and Sparks et al. (7). In the second group of procedures, Compton scatter is used to estimate mass absorption coefficients (13,14,15,16,17). In the last group of techniques, all corrections are made mathematically from a knowledge of fundamental parameters (18). This method requires observation of the intensities of the radiation from all of the major elements in the sample.

Although any one of the matrix correction procedures listed above may work for a particular analytical problem, a combination of two or even all three is justified in a laboratory with a wide variety of sample types. All these procedures require the use of a satisfactory background correction. Since the background is due not only to the mass absorption coefficient and to elemental concentrations of the sample but also to the exciting source, the detector, and the analyzing system, it may well be the limiting factor in the precision of analysis, especially for trace elements in most materials. A good discussion of these problems is presented in a recent review by Russ (19).

The coal analyst must be familiar with all of these problems inherent in X-ray procedures. Most of them can be handled satisfactorily with computer programs. When samples are properly prepared, the analyst can handle types ranging from liquids to solids and from almost pure organic materials to totally inorganic minerals. Such samples can be analyzed 'as is' as long as the surface presented to the spectrometer is uniform, representative, and exhibits no particle-size effects. This may require the use of samples with particles of less than -325 mesh down to a few microns in size especially for the determination of elements of low atomic weight.

Precision for modern X-ray systems is approximately 5% to 25% overall, for trace elements, depending upon the optimization of the spectrograph for the elements of interest. For major and minor elements, depending upon the system used, precision may well be less than 1%. The elements with lower atomic numbers, i.e., Na thru Ca, can not be analyzed as precisely as the heavier elements, especially with energy-dispersive systems.

The limit of detection by X-ray analysis, with presently available commercial equipment, ranges, for coal samples, from 100 for sodium to .5 to 4 PPM for the elements iron through cerium (10). For those elements of heavier atomic weight where the L series X-rays are used for analysis, the limit of detection is approximately 10.

While precision and limit of detection do not necessarily indicate accuracy, with good standards and good programs for matrix corrections the results of X-ray analysis compare favorably with results by other methods of analysis. Its simplicity and ease of operation make it the method of choice where a large number of samples are to be investigated for many elements.

REFERENCES

(1) Kuhn, J. K., Harfst, W. F., Shimp, N. F., "X-Ray Fluorescence Analysis of Whole Coal," Advances in Chemistry 141, 66-73 (1975).

(2) Sweatman, T. R., Norrish, K., Durie, R. A., CSIRO Misc. Rept. 177, 30 pp. (1963).

(3) Rose, H. J., Alder, I., Flanagan, F. J., U.S. Geological Survey Prof. Papers 450-B, 80-82 (1962).

(4) Berman, M., Ergun, S., Bureau Mines Rept. Invest. 7124, 20 pp. (1968).

(5) Kuhn, J. K., "Trace Elements in Whole Coal Determined by X-Ray Fluorescence," Norelco Reporter 20, 3 (1973).

(6) Giauque, R. D., Jaklevic, J. M., "Rapid Quantative Analysis by X-Ray Spectroscopy," Advances in X-Ray Analysis 15, pp. 164-174 (1971).

(7) Sparks, C. J., Ogle, J. C., "Quantitative Trace Element Analysis With X-Ray Fluorescence," First Annual N.S.F. Trace Contaminants Conf., ORNL Conf. 730802 pp. 421-439 (1973).

(8) Blokhim, M. A., "Methods of Spectrochemical Research," Trans. from Russian by F. L. Curzon, Pergamon Press, pp. 344-346 (1965).

(9) ASTM Standards, Annual Book, Part 26, pp. 269-283 (1976).

(10) Ruch, R. R., Gluskoter, H. J., Shimp, N. F., Ill. Geol. Survey, Environmental Geology Note No. 61, 43 p. (1973).

(11) Claisse, F., "Accurate X-Ray Fluorescence Analysis Without Internal Standard," Norelco Reporter 3, 3 (1957).

(12) Lubecki, A., "Theoretical Discussion of Methods of Elimination of Matrix Effects in Non-Dispersive X-Ray Analysis," J. Radioanal. Chem. 2, 3-18 (1969).

(13) Reynolds, R. C., "Matrix Corrections in Trace Element Analysis by X-Ray Fluorescence: Estimation of the Mass Absorption Coefficient by Compton Scatter," Amer. Mineral. 48, 1133-1143 (1963).

(14) Reynolds, R. C., "Estimation of Mass Absorption Coefficient by Compton Scattering: Improvements and Extensions of the Method," Amer. Mineral. 52, 1493-1502 (1967).

(15) Walker, D., "Behavior of X-Ray Mass Absorption Coefficients Near Absorption Edges: Reynolds Method Revisited," Amer. Mineral. 58, 1069-1072 (1973).

(16) Victoreen, J., "The Absorption of Incident Quanta by Atoms as Defined by the Mass Photoelectric Absorption Coefficient and the Mass Scattering Coefficients," J. Applied Physics. 19, 855-860 (1948).

(17) Victoreen, J., "The Calculation of X-Ray Mass Absorption Coefficients," J. Applied Physics 19, 1141-1147 (1949).

(18) Criss, J. W., Birks, L. S., "Calculation Methods for Fluorescent X-Ray Spectrometry," Anal. Chem. 40, 1080-1086 (1968).

(19) Russ, J. C., "Processing of Energy-Dispersive X-Ray Spectra," X-Ray Spectrometry 6, 1 (1977).

X-ray Fluoresence Analysis of Trace
Metals in Solvent Refined Coal

J. W. Prather, A. R. Tarrer and J. A. Guin

Chemical Engineering Department
Auburn University
Auburn, Alabama 36830

Introduction

This work was undertaken to ascertain the ability of Energy Dispersive X-ray
Fluoresence (EDXRF) analysis to determine trace element content of Solvent Refined
Coal (SRC). As a result of recent improvements in the design of solid state detec-
tors for X-ray Fluoresence it is now possible to do very rapid simultaneous quan-
titative analysis of a large number of elements. In this work some 17 elements
are quantitatively analyzed in both raw feed coal and product SRC from the Wilson-
ville SRC Pilot Plant, Wilsonville, Alabama.

The content of trace metals in SRC product and in feed coal is important for
several reasons: Certain metals, particularly iron, catalyze the hydrogenation and
hydrodesulfurization reactions that occur in the SRC process. If the SRC product
is to be used to fire a gas turbine, then trace metals such as Ca, Na, and V present
potential corrosion or fouling problems. When the feed coal has a high oxygen and
a low sulfur content, a substantial portion of western, sub-bituminous coal, for
example, has a low sulfur (~0.7%) and a high oxygen (~17%) content, trace metals
such as Ca react with CO_2 formed in the SRC dissolver and tend to collect in the
dissolver, eventually resulting in plugging problems. Trace metals such as As in
SRC product present potential environmental problems. Also, metals such as Fe and
Al are present in sufficient quantity in the feed coal that the SRC mineral residue
represents an attractive source of these metals when current sources have been
depleted.

Analysis of trace elements in coal has been the subject of many earlier papers
(1,2,3). In fact, analytical methods, specifically, atomic absorption, (4,5) have
been presented for determining the content of trace metals in clean coal products
such as SRC product. However, because of the large number of analyses required to
maintain reasonable quality control of SRC product, etc., alternative methods that
are hopefully more rapid and less expensive than those currently available are
needed. Application of EDXRF to perform assays of feed coals and SRC products is
attractive because it allows simultaneous analysis of trace elements found in feed
coals and SRC products. This work demonstrates that EDXRF is an effective method
for determining the content of trace metals in coal and coal-dérived products.

Experimental

Equipment

All EDXRF analyses were done on a Kevex 0810RW X-ray Fluoresence System (Kevex
Corporation, Burlingame, Ca. 94010) consisting of a 0810A X-ray Subsystem, 5100C
analyzer, 5100 X-ray Spectrometer Rigaku Gigerflex 3kW X-ray generator, (60 kV and
180 ma) Digital Electronics Corporation PDP 11/03 Computer with RX01 dual floppy
disk bulk storage. The system uses a high power X-ray tube (Ag target) to produce
x-rays from a series of selectable secondary targets (Ti, Ge, Mo, and Sn). The
spectrometer uses a solid state detector of 30 mm^2 active area that has resolution
of <165eV @ 1KHz.

Atomic Absorption experiments for iron were done on a Perkin-Elmer Model 305A
Atomic Absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut
06856) using an acetylene/air flame and a wavelength setting of 249 nm. Sulfur
determinations were made using a Leco model 521-500 sulfur analyzer specially fitted
for low level sulfur detection (Laboratory Equipment Corporation, St. Joseph, Michi-
gan 49085).

Procedure

Approximately 10 g. samples of all coals and SRC's were first ground so that the entire sample passed through a 325 mesh screen. The samples were then dried in a vacuum oven at 105°C for at least 3 hours. From these samples 1.25 inch pellets were made using a boric acid backing and were analyzed by EDXRF under a vacuum of 5 x 10^{-4} torr. Also, fractions of the same samples were used to perform Leco sulfur, C, H and N, and Atomic Absorption analyses.

The raw EDXRF data were analyzed using the Kevex matrix correction program, and adaptation of the shell EXACT (6) program. The EXACT program employs a fundamental parametric method which accounts for matrix interactions due to absorption and enhancement for all the elements in the sample. The EXACT model is basically similar to models presented by Sherman (7), Shiraiwa (8) and Criss and Birks (9) with simplifications.

Results

Table 1 gives a comparison between EDXRF and two methods, Atomic Absorption (AA) and Leco, commonly used in this laboratory for analysis of iron and sulfur, respectively. At the bottom of Table 1 are analyses for three standards (Certified Atomic Absorption Standard, 1000 ppm iron, Fisher Scientific, FairLawn, New Jersey 07410; Calibration Standard no. 764-547 (2.02 ± 0.03% S) and Calibration Standard no. 764-545 (0.31 ± 0.02% S) LECO Corporation, 3000 Lakeview, St. Joseph, Michigan 49085). These standards were purchased for use in calibration of atomic absorption and LECO analysis. In all cases EDXRF gave the best accuracy for the standards analysis.

Table 2 gives the EDXRF elemental analyses for 12 coals and SRC's. As expected smaller amounts of the 17 elements analyzed for were detected in the SRC products than in the respective feed coals.

Little would actually be gained by an element by element comparison of the various coals and SRC's. On the other hand, Figure 1 gives an interesting correlation between ash content of moisture free coal and cumulative weight percent of 15 elements (Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, and Sr) as determined by EDXRF. Least Squares analysis of the data gave a straight line correlation factor (r) of 0.92 at the 95% confidence level. An r value of 0.92 indicates a reasonable fit was obtained and that the resulting correlation can be used to compute the approximate percent ash in feed coals. Most importantly, these data demonstrate that the ash content of a feed coal can be approximated very rapidly in this manner. At this time experiments are in progress to show that the same relationship is also true for SRC product.

Summary and Conclusion

It has been shown that EDXRF is capable of analyzing coals and SRC's for elemental content. These analyses provide simultaneous results for several important elements, namely sulfur, iron and calcium, as well as percent ash. These analyses presently take well over 2 hours per sample to complete, but by using EDXRF this time can be reduced to less than one hour per sample. Furthermore, EDXRF has an added feature in that it may be automated, leading to even shorter analysis times per sample. Thus, EDXRF can be concluded to be an effective tool that can provide very accurate and rapid analyses of coals and SRC product for their elemental content.

Acknowledgement

TABLE 1

Comparison of EDXRF to Atomic Absorption and Leco Sulfur

Coal	XRF	A.A.	Leco	Known Value
Western Kentucky				
Fe	0.697	0.800		
S	2.24		2.56	
Wyodak				
Fe	0.265	0.247		
S	0.637		0.764	
Illinois #6				
Fe	0.629	0.526		
S	2.76		2.45	
Pittsburg #8				
Fe	0.561	0.615		
S	2.22		2.87	
Monterrey				
Fe	1.165	0.732	.	
S	3.07		3.24	
Rosebud				
Fe	0.466	0.270		
S	0.976		1.04	
Bighorn				
Fe	0.267	0.216		
S	0.582		0.620	
Standards				
Fe	0.1072	0.937		0.1000
S	1.995		2.22	2.02
S	0.301		0.278	0.31

Literature Cited

1. M. Berman and S. Ergun, Fuel, 47, 285 (1968).

2. T. R. Sweatman, K. Norrish and R. A. Durie, CSRIO Misc. Rep., No. 177 (1963).

3. L. T. Kiss, Anal. Chem., 38, 1731 (1966).

4. H. Schultz, G. A. Gibbon, E. A. Hultman, H. B. Booher, and J. W. Adkins, PERC/RI-44/2, (1977).

5. W. M. Coleman, P. Szabo, D. L. Wooton, H. C. Dorn and L. T. Taylor, Preprints Fuel Division, 173rd National A.C.S. Meeting, New Orleans, La., 22, 226 (1977).

6. J. W. Otvos, G. Wyldand, T. C. Yao, 25th Annual Denver X-ray Conference (1976).

7. J. Sherman, Spectrochimica Acta, 7, 283 (1955).

8. J. Shiraiwa, N. Fugino, Japan J. Appl. Phys., 5, 886 (1966).

9. J. W. Criss and L. S. Birks, Anal. Chem., 40, 1080 (1968).

TABLE 2

EDXRF Analysis of SRC and Coal

Element	A	B	wt.% C	D	E	F
Si		1.612		1.813		2.097
P	0.0755	0.183	0.0657	0.186	0.0840	0.251
S	0.723	2.24	1.04	2.22	0.755	2.76
Cl	0.0097	0.0177	0.0053	0.105		
K	0.001	0.0977		0.100		0.112
Ca	0.0087	0.0817	0.0144	0.910	0.0024	0.148
Ti	0.0092	0.0383	0.0088	0.0537	0.0178	0.0549
V	0.0037	0.0089	0.0049	0.0099	0.0036	0.0149
Cr		0.0036	0.0026	0.0025	0.0023	0.0058
Mn	0.0018	0.0022	0.0008	0.0043	0.0026	0.0048
Fe	0.0427	0.697	0.0191	0.561	0.0199	0.629
Ni	0.0002	0.0010	0.0008	0.0038	0.0010	0.0020
Cu	0.0003	0.0012	0.0006	0.0028	0.0014	0.0017
Zn	0.0005	0.0013	0.0007	0.0038	0.0006	0.0015
As	0.0001	0.0008	0.0002	0.0005	0.0001	0.0006
Br	0.0002	0.0003	0.0004	0.0009	0.0003	0.0005
Sr		0.0014		0.0132		0.0014

A   Western Kentucky SRC
B   Western Kentucky 9/14 Coal
C   Pittsburg #8 SRC
D   Pittsburg #8 Coal
E   Illinois #6 SRC
F   Illinois #6 Coal

TABLE 2 CONTINUED

EDXRF Analysis of SRC and Coal

Element	G	H	wt.% I	J	K	L
Si		1.073	0.1021	2.578	0.821	0.903
P	0.0306	0.143	0.0953	0.2193	0.122	0.101
S	0.152	0.6371	1.172	3.070	0.976	0.582
Cl	0.0036	0.0536		0.241	0.106	
K		0.0310	0.0040	0.1245	0.0266	0.0204
Ca	0.0162	0.858	0.0022	0.2750	0.557	0.473
Ti	0.0078	0.0585	0.0133	0.0617	0.0352	0.0511
V	0.0023	0.0353	0.0034	0.0104	0.0124	
Cr	0.0017	0.0033		0.0090	0.0110	0.0041
Mn	0.0012	0.0031		0.0087	0.0063	0.0025
Fe	0.0228	0.2615	0.0450	0.1651	0.466	0.2667
Ni	0.0013	0.0006		0.0015	0.0019	0.0014
Cu	0.0017	0.0056	0.0010	0.0201	0.0017	0.0058
Zn	0.0005	0.0020	0.0004	0.0016	0.0004	0.0013
As	0.0001	0.0004	0.0001	0.0006	0.0003	0.0005
Br		0.0002	0.0004	0.0005	0.0008	0.0001
Sr	0.0001	0.0137	0.0007	0.0013	0.0088	0.0074

G   Wyodak (Amax) SRC
H   Wyodak (Amax) Coal
I   Illinois (Monterrey) SRC
J   Illinois (Monterrey) Coal
K   Rosebud Coal
L   Big Horn Coal

FIGURE 1